

# **Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 3 Topical Report**

**Topical Report, June 2001**

# **Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 3 Topical Report**

Topical Report, June 2001

U.S. Department of Energy Project Manager

Peter Botros

EPRI Project Manager

Richard Rhudy

## DISCLAIMER

---

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

# CITATIONS

This document was prepared by

URS Group  
9400 Amberglenn Boulevard  
Austin, Texas 78729

Principal Investigators

G. Blythe  
B. Marsh  
S. Miller  
C. Richardson  
M. Richardson

This document describes research sponsored by EPRI and the U.S. Department of Energy.

The publication is a corporate document that should be cited in the literature in the following manner:

*Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 3 Topical Report*,  
EPRI, Palo Alto, California, U.S. Department of Energy, National Energy Technology  
Laboratory, Pittsburgh, Pennsylvania: 2001.

## **ABSTRACT**

The U.S. Department of Energy and EPRI have co-funded this project to improve the control of mercury emissions from coal-fired power plants equipped with wet flue gas desulfurization (FGD) systems. The project investigated catalytic oxidation of vapor-phase elemental mercury to a form that is more effectively captured in wet FGD systems. If successfully developed, the process could be applicable to over 90,000 MW of utility generating capacity with existing FGD systems and to future FGD installations.

Field tests have been conducted to determine whether candidate catalyst materials remain active towards mercury oxidation after extended flue gas exposure. Catalyst life will have a large impact on the cost effectiveness of this potential process. A mobile catalyst test unit has been used to test the activity of four different catalyst materials for a period of up to six months at each of three utility sites. Catalyst testing was completed at the first site, which fires Texas lignite, in December 1998 and at the second test site, which fires a Powder River Basin subbituminous coal in the fall of 1999. Testing at the third site, which fires a medium- to high-sulfur bituminous coal, began in June 2000 and was completed at the end of January 2001.

This Topical Reports includes results from Site 3; results from Sites 1 and 2 were reported previously. At Site 3, catalysts were tested in two forms, including powders dispersed in sand bed reactors and in a commercially available form as a coated honeycomb structure.

Field testing has been supported by laboratory tests to screen catalysts for activity at specific flue gas compositions, to investigate catalyst deactivation mechanisms and methods for regenerating spent catalysts. Laboratory results related to the Site 3 field effort are also included and discussed in this Topical Report.

# CONTENTS

<b>1 INTRODUCTION.....</b>	<b>1-1</b>
<b>2 PHASE II TECHNICAL APPROACH.....</b>	<b>2-1</b>
Field Test Program.....	2-1
Commercial Catalyst Form Tests .....	2-3
Laboratory Tests .....	2-4
Phase II Status.....	2-5
References.....	2-5
<b>3 SITE 3 RESULTS .....</b>	<b>3-1</b>
Site 3 Description .....	3-1
Site Selection .....	3-2
Short-term Catalyst Screening Test Results .....	3-3
Long-term Test Results.....	3-8
Commercial Catalyst Form Tests .....	3-18
Flue Gas Characterization Results.....	3-20
Flue Gas Mercury Concentrations .....	3-21
Other Metals in the Flue Gas .....	3-24
Halogens in the Flue Gas .....	3-26
Flue Gas SO <sub>3</sub> Concentration .....	3-26
Coal and Fly Ash Analyses .....	3-30
Continuous Monitoring for Flue Gas Mercury Content.....	3-34
Process Correlations.....	3-37
<b>4 LABORATORY TEST RESULTS .....</b>	<b>4-1</b>
Catalyst Screening Tests .....	4-1
Catalyst Regeneration Tests .....	4-3
Laboratory Testing of Site 3 Long-term Catalysts .....	4-3
Catalyst Regeneration .....	4-6
Investigation of Catalyst Deactivation Mechanisms .....	4-6
Leaching of Water-soluble Acids from Catalyst Materials .....	4-7
Trace Metals Analyses of Recovered and Regenerated Catalysts .....	4-9
References.....	4-14

<b>5 PRELIMINARY ECONOMICS FOR A CATALYTIC PROCESS .....</b>	<b>5-1</b>
References.....	5-3
<b>6 SUMMARY.....</b>	<b>6-1</b>
<b>7 ACKNOWLEDGEMENTS .....</b>	<b>7-1</b>

# LIST OF FIGURES

---

Figure 2-1 Schematic of Field Test Unit and Semi-continuous Mercury Analyzer.....	2-2
Figure 3-1 Flue Gas Flow Configuration at Site 3.....	3-1
Figure 3-2 Observed Decrease in Measured Elemental Mercury Concentrations over Time at Site 3.....	3-15
Figure 3-3 Apparent Elemental Mercury Oxidation Percentage vs. Time in Operation for the Sand Bed Blank in the Long-term Test Apparatus.....	3-16
Figure 3-4 Long-term Catalyst Oxidation Results from Site 3.....	3-17
Figure 3-5 Sample Locations Located Upstream of the ID Fans .....	3-35
Figure 3-6 Sample Locations Located Downstream of the ID Fans.....	3-35
Figure 3-7 Mercury Concentration/Speciation at Air heater Inlet and Outlet.....	3-36
Figure 3-8 Mercury Concentration/Speciation ESP Inlet and Outlet .....	3-37
Figure 3-9 Mercury Concentration/Speciation at FGD Inlet and Outlet.....	3-38
Figure 3-10 Relationship between Coal Mercury Content and Flue Gas Mercury Concentrations at the FGD Inlet .....	3-38
Figure 3-11 FGD Inlet Total Mercury by SCEM vs. Coal Flow and Unit Load.....	3-40
Figure 3-12 Results of Simultaneous FGD Inlet and Outlet Gas Monitoring for Total Mercury Concentration by Mercury SCEM .....	3-40
Figure 3-13 Relationship between Opacity and Flue Gas Mercury Concentrations at the FGD Inlet .....	3-41



# LIST OF TABLES

---

Table 3-1 Mercury Adsorption Data from the Short-term Tests at Site 3 .....	3-5
Table 3-2 Elemental Mercury Oxidation Data from the Short-term Tests at Site 3.....	3-6
Table 3-3 Catalyst Materials Selected for Testing in the Long-term Test at Site 3.....	3-8
Table 3-4 Mercury Adsorption Data from the Long-term Test at Site 3, October 2000 .....	3-9
Table 3-5 Elemental Mercury Oxidation Data from the Long-term Test at Site 3, October 2000.....	3-10
Table 3-6 Mercury Adsorption Data from the Long-term Test at Site 3, November 2000.....	3-11
Table 3-7 Elemental Mercury Oxidation Data from the Long-term Test at Site 3, November 2000 .....	3-11
Table 3-8 Mercury Adsorption Data from the Long-term Test at Site 3, December 2000.....	3-12
Table 3-9 Elemental Mercury Oxidation Data from the Long-term Test at Site 3, December 2000 .....	3-13
Table 3-10 Mercury Adsorption Data from the Long-term Test at Site 3, January 2001 .....	3-14
Table 3-11 November Mercury Adsorption Data from the Honeycomb Sample Test at Site 3.....	3-18
Table 3-12 November Elemental Mercury Oxidation Data from the Honeycomb Sample Test at Site 3.....	3-18
Table 3-13 Results of Ontario Hydro Mercury Measurements at Site 3, July 2000.....	3-21
Table 3-14 Method 29 Mercury Results for the FGD Inlet Location .....	3-22
Table 3-15 Ontario Hydro Method Results from Site 3, January 2001 .....	3-23
Table 3-16 Method 29 Metals Results for the FGD Inlet Location .....	3-25
Table 3-17 Method 26A Sampling Results for the FGD Inlet Location.....	3-26
Table 3-18 Controlled Condensation System Sampling Results for the FGD Inlet and Outlet Locations, July 2000 .....	3-26
Table 3-19 Results of CCS Measurements Made at Site 3 During January 2001.....	3-28
Table 3-20 Results of Mercury Analysis of Site 3 Coal and Fly Ash Samples .....	3-31
Table 3-21 Results of LOI Analyses on Fly Ash Samples from June through November 2000.....	3-32
Table 3-22 Results of Ultimate Analyses of Coal Samples from Site 3 (all values as received basis).....	3-32
Table 3-23 Summary of Mercury Balance Calculations for Site 3, June 2000 through January 2001 .....	3-33
Table 4-1 Simulated Flue Gas Compositions for Bench-Scale Tests .....	4-1
Table 4-2 Laboratory Oxidation Test Results at Three Simulation Gas Temperatures .....	4-2

Table 4-3 Comparison of Laboratory Oxidation Test Results at 300°F (149°C) with Site 3 Short-term Screening Test Results .....	4-4
Table 4-4 Comparison of Laboratory Test Results for Recovered Catalysts to Site 3 Long Term Results.....	4-4
Table 4-5 Catalyst Activity Results for Regenerated Catalyst Samples from Site 3 .....	4-6
Table 4-6 Acid Leaching from Recovered Catalyst Samples into Deionized Water .....	4-7
Table 4-7 Acid Leaching from Site 3 Fly Ash Samples into Deionized Water .....	4-9
Table 4-8 Trace Metal Concentrations in Catalyst/Sand Beds Recovered from Site 3 Long-term Test.....	4-10
Table 4-9 Trace Metals Analyses of Site 3 Catalysts – Pre and Post Regeneration .....	4-12
Table 4-10 Comparison of Selenium Concentrations for Catalyst Materials from Long- term Tests at Sites 1 and 3 .....	4-13
Table 4-11 Comparison of Selenium Desorption Versus Activity Towards Elemental Mercury Oxidation in Regenerated Site 3 Catalysts .....	4-14
Table 5-1 Preliminary Cost Estimates for the Catalytic Process for Enhancing Mercury Removal by a Wet FGD System, Compared to Activated Carbon Injection .....	5-3

# 1

## INTRODUCTION

The 1990 Clean Air Act Amendments mandated the Environmental Protection Agency to study the health effects caused by hazardous air pollutants (HAPs) from electric utility plants, including a separate study of the effect of mercury emissions. Most HAPs of concern in power plants occur in the particulate phase and are therefore removed in particulate control devices. However, mercury, although present in extremely low concentrations, primarily occurs in the vapor phase. Therefore, particulate removal devices are generally not effective at removing mercury from flue gas and alternative removal methods are needed. A number of previous research programs have studied mercury emissions from power plants and methods for reducing these emissions.

The U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) is funding this project to investigate a process for improving the ability of existing wet FGD systems to control mercury emissions from coal-fired power plants. The project is being conducted under a cost-sharing PRDA agreement between DOE/NETL, EPRI and URS Corporation (formerly Radian International LLC). The proposed process would use a catalyst material to oxidize vapor-phase elemental mercury. Vapor-phase mercury generally exists in two forms in utility flue gas—as elemental mercury and as water soluble, oxidized mercury (the predominant form is believed to be  $\text{HgCl}_2$ ). Previous results have shown that wet scrubbers effectively remove oxidized mercury from the gas but are ineffective at removing elemental mercury. Since elemental mercury is present in most flue gas streams and is the predominant form in some, this process can potentially improve overall mercury removal in wet scrubbers by converting the elemental mercury to a form that is more readily scrubbed.

This project is being conducted in two phases. During Phase I, several catalyst materials were identified in the laboratory as being able to oxidize elemental mercury. This ability was confirmed in pilot-scale tests and in short-term, slipstream field tests. Pilot tests also confirmed the removal of catalytically oxidized mercury across a wet FGD system. Phase II began in April 1998, and is investigating catalyst life by exposing catalyst materials to flue gas for an extended period of time at three coal-fired power plants. This testing will be used to predict required catalyst quantities and catalyst life for future full-scale application of the technology.

Section 2 of this technical note describes the technical approach for Phase II and Section 3 presents Phase II results from the third site. In Section 4, the results of related laboratory testing are presented, and preliminary economics for the catalyst process are presented and discussed in Section 5. A summary of the Site 3 results is made in Section 6, and acknowledgements are made in Section 7.

# 2

## PHASE II TECHNICAL APPROACH

Based on promising Phase I results, DOE/NETL funded a Phase II effort, which includes:

- Evaluate the ability of catalyst materials to oxidize elemental mercury at three full-scale sites;
- Estimate the life of these catalyst materials in various flue gas streams; and
- Estimate the amount of catalyst required to achieve at least 70% oxidation of the elemental mercury in these flue gas streams.

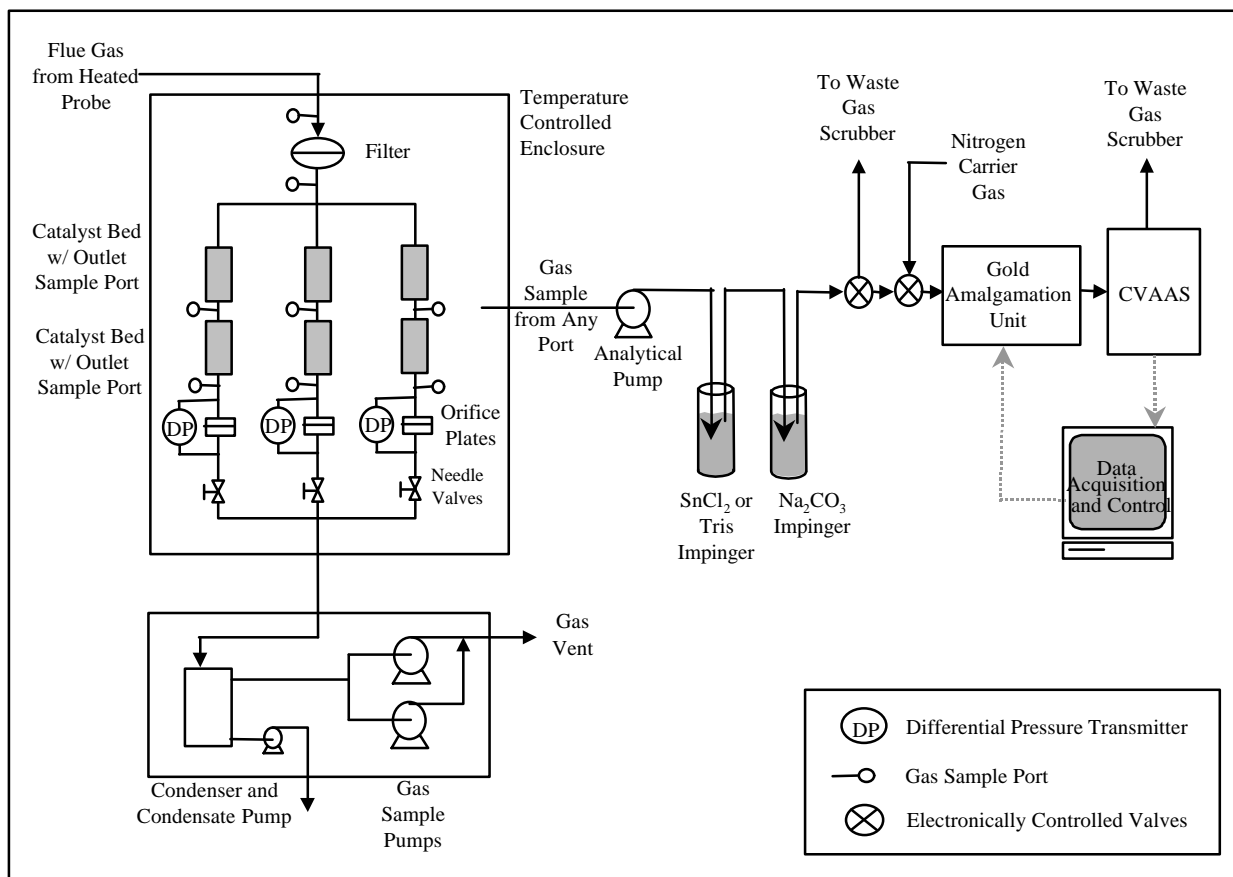
Phase II testing is addressing two critical issues – the life of the catalysts (i.e., how long will the catalysts oxidize mercury?) and the applicability of the process for the U.S. electric utility industry (i.e., are there coals/plants for which the catalysts work more or less effectively?). These issues are being addressed by conducting long-term catalyst tests at three full-scale utility sites. Catalyst oxidation efficiency and life will ultimately affect the design of any subsequent commercial process and its economics. Also included in Phase II are field tests of “advanced” or commercial catalyst forms, and laboratory related laboratory testing. Each form of testing is described below.

### Field Test Program

Figure 2-1 illustrates the catalyst test unit, which was designed to expose catalyst materials to a slipstream of flue gas from a coal-fired boiler for an extended period. The test unit consists of a heated box that is mounted directly to a flue gas duct, and is small enough to be moved from site to site. Flue gas is continuously drawn from the duct through a heated glass probe and passes through a quartz filter before contacting the catalyst beds. Although in future full-scale systems, the catalyst would be exposed to fly ash remaining in the flue gas downstream of the particulate control device, residual fly ash is removed in the test unit to prevent plugging of the sand beds. A commercial catalyst configuration (e.g., a honeycomb) would be designed to avoid plugging with ash.

After the filter, the flue gas flows through three parallel catalyst test cells. Each test cell contains two packed beds of catalyst material. Catalyst bed temperatures are controlled by adjusting temperatures in the heated box. The gas flow rate through each test cell is continuously monitored, and gas flow rates are adjusted with manual valves. After flowing through the cells, the flue gas passes through a condenser to remove moisture then to sample pumps. At the normal flue gas flow rate, the superficial gas velocity through a test cell is about 18 ft/min (0.1 m/s), which is similar to the gas velocity through a fabric filter in the EPRI COHPAC configuration (i.e., a high-ratio pulse-jet fabric filter installed downstream of an ESP).

There are two catalyst beds in series in each of the three test cells, so up to six different catalyst materials can potentially be tested simultaneously. However, one bed typically contains a sand



**Figure 2-1**  
**Schematic of Field Test Unit and Semi-continuous Mercury Analyzer**

bed “blank,” and another cell typically has two beds containing the same catalyst material in series, to provide oxidation data at two space velocities (i.e., different ratios of gas flow rate to catalyst volume). Consequently, only four different catalyst materials are typically tested at once.

The catalyst materials in the test cells are diluted with sand. The sand improves gas flow distribution by providing a thicker bed and greater gas pressure drop. Test ports are located at the outlet of each catalyst bed and at the inlet and outlet of the quartz filter. Mercury samples can be collected upstream and downstream of all catalyst beds. By measuring the change in elemental mercury concentration across each bed, the mercury oxidation across each can be determined.

Mercury measurements are made using a semi-continuous mercury analyzer developed for EPRI. As shown in Figure 2-1, flue gas is pulled from the catalyst test unit at about 1 L/min through a Teflon<sup>®</sup>-lined pump and passes through a series of impingers. To measure total mercury in the flue gas, the impinger solutions contain stannous chloride ( $\text{SnCl}_2$ ) followed by a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) buffer. The  $\text{SnCl}_2$  solution reduces all flue gas mercury species to elemental mercury. The  $\text{Na}_2\text{CO}_3$  solution removes acid gases, thus protecting the downstream, analytical gold surface. Gas exiting the impingers flows through a gold amalgamation column where mercury in the gas is adsorbed. After concentrating mercury onto the gold for a fixed period of

time (typically 10 minutes), the mercury is thermally desorbed ( $>700^{\circ}\text{C}$ ) from the column into a nitrogen purge stream that flows to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. The flue gas total mercury concentration is measured semi-continuously with a 10-minute sample time followed by a 10-minute analysis period.

To measure elemental mercury in the flue gas, the  $\text{SnCl}_2$  impinger is replaced with one containing tris(hydroxymethyl)aminomethane (Tris) solution. The Tris solution has been shown to capture oxidized mercury while allowing elemental mercury to pass through without being altered<sup>1</sup>. Mercury passing through the Tris solution is analyzed as described above and assumed to represent the elemental mercury content in the gas sampled. The difference between the total mercury concentration (stannous chloride impinger train) and elemental mercury concentration (Tris impinger train) is taken as the oxidized mercury concentration. The analyzer results have been confirmed at each site by performing manual sampling by the draft Ontario Hydro method.

The most promising catalyst materials are being tested for up to six months at each of three utility power plants. At each site, an initial set of short-term screening tests is conducted to determine the most active catalysts for that site and to allow comparing the performance of several catalyst materials from site to site. Each screening test is run for two to four days, to allow the catalysts to approach mercury adsorption equilibrium before measuring oxidation performance. Based on the screening test results, four catalyst materials are selected for continuous long-term (five- to six-month) flue gas testing at each site. Periodic performance measurements are taken to determine if oxidation has changed with time. Between performance measurements, the test unit operating conditions are monitored remotely using mobile communications. This approach has been used to measure catalyst life for four catalyst materials at three coal-fired facilities.

The test sites were chosen to provide a range of flue gas compositions and correspond with the three solid fossil fuels used for power generation in the U.S.: bituminous coal, subbituminous coal, and lignite. Of the installed FGD capacity in the U.S., about 48% (on a megawatt basis) is on power plants that fire bituminous coal, 40% on plants that fire subbituminous coal, and 12% on plants that fire lignite. Testing has been completed at all three sites. The first site fires a medium-sulfur Texas lignite, the second site fires a low-sulfur Powder River Basin subbituminous coal, and the third site fires a medium- to high-sulfur bituminous coal.

## **Commercial Catalyst Form Tests**

During the long-term testing of catalyst sand beds at Site 3, additional tests were conducted to evaluate the activity of a catalyst material wash coated onto a honeycomb support such as is used in flue gas  $\text{NO}_x$  selective catalytic reduction (SCR). The objective of these tests was to evaluate promising catalysts identified in the long-term tests in a commercially available configuration.

These tests were conducted in an apparatus operated in parallel with the long-term field test unit described above. The honeycomb catalyst test apparatus drew flue gas from a quartz-lined probe installed in a port next to that of the long-term field test unit. Flue gas was drawn through heated Teflon<sup>®</sup> sample lines to one or more Teflon<sup>®</sup> catalyst holders placed in a temperature-controlled, heated box. Flue gas flow rates were measured with a calibrated rotameter on a periodic basis. Mercury concentrations were measured upstream and downstream of each catalyst holder using

the field analytical instrument described above. These analyses were conducted when the analyzer was not being used to measure mercury concentrations for the long-term field test unit.

The catalyst holders contained 5/8-in. (16-mm) diameter “cores” of catalyst material wash coated on a honeycomb alumina support. These catalyst forms were tested over relatively short time periods (i.e., days rather than weeks), as the primary objective of these tests was to measure activity in this configuration rather than catalyst life.

The testing was focused on flue gas flow rates that would correspond with commercially viable catalyst reactor sizes. If we assume that mercury oxidation occurs primarily on the external surfaces of the catalyst materials (i.e., not in the pores), the design term “area velocity” probably represents the best parameter for scaling small-scale reactor results to a commercial catalyst bed design. Area velocity is calculated as the flue gas flow rate at standard conditions divided by the catalyst material’s geometric (external) surface area. SCR catalysts typically operate at area velocities ranging from 15 to 30 standard ft/hr (4.3 to 8.7 Nm/hr). If mercury catalysts can be proven effective at similar or higher area velocities, it is likely that honeycomb support structures could be utilized in a reactor of a commercially viable size. The actual area velocities tested for honeycomb catalysts at Site 3 ranged from approximately 90 to 170 standard ft/hr (26 to 49 Nm/hr).

## **Laboratory Tests**

Laboratory tests have also been conducted to support the field tests. Typically, a simulated flue gas containing elemental mercury flows across a fixed-bed reactor containing catalyst material. The gas exiting the bed is analyzed semi-continuously by the technique described above to determine the fraction of inlet elemental mercury oxidized across the bed. Mercury speciation across the catalyst bed is determined after adsorption equilibrium is established.

Simulated flue gas is prepared from reagent gases using calibrated flow meters. Elemental mercury is added by passing nitrogen carrier gas across a diffusion cell that contains an elemental mercury permeation tube. The amount of diffused mercury is controlled with the flow of nitrogen and the temperature of the diffusion cell. The mercury-containing nitrogen is then mixed with other flue gas components (SO<sub>2</sub>, HCl, NO<sub>x</sub>, O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O) at constant temperature before the gas enters the reactor.

The fixed-bed reactor is a temperature-controlled, vertical Pyrex column that contains a mixture of the catalyst material and sand. The gas rate is typically about 1.4 L/min at 300°F (149°C), which results in a superficial gas velocity through the bed of about 30 ft/min (0.15 m/s).

The bench-scale unit is used to simulate flue gas conditions at each full-scale test site prior to testing in the field, to obtain information about the expected effects of flue gas composition on mercury oxidation. The bench-scale unit is also being used to investigate the regeneration of spent catalysts. Spent catalysts are regenerated by exposure to various atmospheres at elevated temperatures, then tested for mercury oxidation activity in simulated flue gas. Other tests are run on the bench-scale unit in an effort to develop a better understanding of mercury oxidation and catalyst deactivation mechanisms.

## Phase II Status

Phase II results to date include completed long-term sand bed test series at Sites 1, 2 and 3, screening tests for the activity of commercial catalyst forms at Sites 2 and 3, and laboratory-scale catalyst screening and regeneration tests for all three sites. Sites 1 and 2 results have been reported previously<sup>2,3,4,5,6</sup>, and are not repeated here. This technical note is focused on results from Site 3 and related laboratory tests.

## References

1. Carey, T.R., et al. "Effect of Mercury Speciation on Removal Across Wet FGD Processes." Presented at the AIChE Spring National Meeting, Session 47, New Orleans, LA, February 25-29, 1996.
2. Blythe, G.M., et al. "Enhanced Control of Mercury by Wet FGD Systems." Presented at the AWMA 92<sup>nd</sup> Annual Meeting, St. Louis, MO, June 1999.
3. Richardson, Dr. Carl F., et al. "Enhanced Control of Mercury by Wet FGD Systems." Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, Atlanta, GA, August 16-20, 1999.
4. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 1 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 1999, TE-113397.
5. Richardson, Dr. Carl F., et al. "Enhanced Control of Mercury by Wet FGD Systems." Presented at the AWMA 93<sup>rd</sup> Annual Meeting, Salt Lake City, UT, June 2000.
6. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 2 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 2000. 1000558.



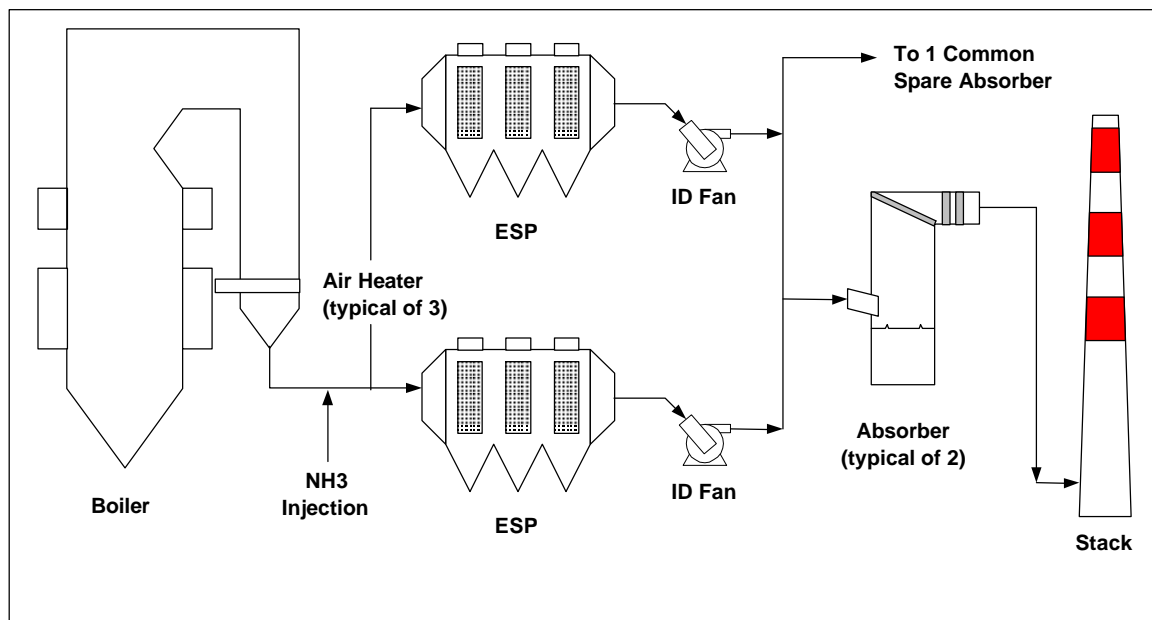
# 3

## SITE 3 RESULTS

This section describes the results of field testing conducted at the third site for this project. The section includes a description of the site and the site selection process. Results are then presented from short-term mercury oxidation catalyst activity tests and long-term activity tests using sand-bed reactors. Results are also presented from short-term tests conducted with commercially available honeycomb catalyst materials. Finally, results are presented from flue gas, coal, and fly ash characterization efforts conducted as part of the test program at Site 3.

### Site 3 Description

Site 3 is a large (>750 MW) tangentially-fired unit that fires a blend of Pennsylvania and West Virginia bituminous coals with an average sulfur content of about 2.6 wt %. It has an ESP for particulate control. An ammonia conditioning system installed in the flue gas path between the air heater and ESP is used to improve ESP performance. The ESP outlet flue gas contains about 1600 to 1700 ppm of SO<sub>2</sub>, and 70 to 80 ppm of HCl. The SO<sub>2</sub> (and HCl) emissions are controlled with a limestone reagent wet flue gas desulfurization (FGD) system. The FGD system was designed for 95% SO<sub>2</sub> removal. All of the flue gas from Site 3 is scrubbed; there is no gas bypass. Figure 3-1 illustrates the flue gas path from the boiler to the stack at Site 3.



**Figure 3-1**  
**Flue Gas Flow Configuration at Site 3**

A bituminous coal plant was selected to host Site 3 because bituminous coal is fired by the greatest number of megawatts of generating capacity among FGD-equipped power plants. As

described below, there was some difficulty in identifying a bituminous coal site that was known to have adequate elemental mercury concentrations in the flue gas to support quantitative oxidation catalyst performance testing.

## Site Selection

The host for Site 3 testing was identified during the first half of the year 2000. This timing was fortunate, as results from the US EPA's mercury Information Collection Request (ICR) were becoming available at this time. The ICR program selected a number of bituminous coal sites equipped with wet FGD to conduct flue gas mercury concentration measurements by the draft Ontario Hydro method, and required all coal-fired units to measure mercury content and other parameters for a representative sampling of their fuels. This provided very useful data for identifying potential host units for Site 3 catalyst testing.

In EPA's mercury ICR program, most bituminous coals were measured to contain about 0.1 ppm (by weight) of mercury, which typically corresponds with about  $10 \mu\text{g}/\text{Nm}^3$  of total mercury<sup>1</sup> in the boiler exit flue gas. Most bituminous coals were observed to produce a flue gas with a highly oxidized mercury content, typically on the order of 80% oxidized or greater. Such coals produce a flue gas with only  $2 \mu\text{g}/\text{Nm}^3$  of elemental mercury or less. At such low elemental mercury concentrations, it is difficult to measure the effectiveness of mercury oxidation catalysts. It would be desirable to identify catalysts capable of achieving at least 90% oxidation of elemental mercury in flue gas. For a flue gas with only  $2 \mu\text{g}/\text{Nm}^3$  of elemental mercury, 90% oxidation would leave only  $0.2 \mu\text{g}/\text{Nm}^3$  of elemental mercury, which is at or below the detection limit for the field mercury analyzer being used to evaluate catalyst performance in this project.

Note that a catalytic oxidation process still may be applicable to bituminous coal fired units, even with total mercury concentrations of  $10 \mu\text{g}/\text{Nm}^3$  and  $2 \mu\text{g}/\text{Nm}^3$  or less of elemental mercury. It will depend on how future mercury control regulations are written as to what level of mercury oxidation may be required such that mercury removal by a wet FGD system will be adequate to achieve compliance. Some plants with naturally occurring mercury oxidation percentages of 80% or greater may require further oxidation to ensure compliance. However, as described above, such sites are not ideal for testing and quantifying catalyst performance because of the low elemental mercury concentrations that result downstream of an effective catalyst.

In March of 2000, a potential host for Site 3 was identified, that fires a high-sulfur Indiana bituminous coal with approximately 0.1 ppm of mercury content. Project team members traveled to the site to measure flue gas mercury concentrations at the FGD inlet location by the draft Ontario Hydro method. These measurements showed  $9.7 \mu\text{g}/\text{Nm}^3$  of total mercury and  $1.5 \mu\text{g}/\text{Nm}^3$  of elemental mercury in the flue gas at that location. As described above, this elemental mercury concentration was seen as being too low to support effective catalyst evaluation.

In the EPA ICR data, a number of coals from Ohio and Pennsylvania were reported to contain, on average, much higher concentrations of 0.2 to 0.3 ppm of mercury or greater. The flue gases from firing these coals were expected to contain  $20 \mu\text{g}/\text{Nm}^3$  to  $30 \mu\text{g}/\text{Nm}^3$  of total mercury. Even

---

<sup>1</sup> Throughout this report, flue gas mercury concentrations are reported in units of  $\mu\text{g}/\text{Nm}^3$ . For comparison purposes, note that  $10 \mu\text{g}/\text{Nm}^3$  of mercury is equivalent to a flue gas concentration of approximately 1.1 ppb (by volume).

with 80% mercury oxidation, these flue gases should contain approximately 4 to 6  $\mu\text{g}/\text{Nm}^3$  of elemental mercury, which would be within the desired range for Site 3 catalyst testing.

Project team members contacted two utilities that fire such Ohio or Pennsylvania bituminous coals and that have existing FGD systems. An initial, positive response was received from one of the two sites, with two large (>750 MW) boilers that fire a Pennsylvania and West Virginia coal blend. In late May, the utility confirmed they were willing to host Site 3 at this station.

In early June, the equipment needed to conduct testing at this Site 3 was mobilized and shipped to the site. The equipment arrived at Site 3 on June 13. Equipment setup began on June 14, and the first short-term catalyst screening test began on June 16.

The flue gas mercury concentrations, as determined by the EPRI semi-continuous flue gas mercury analyzer, were lower than expected. Total mercury concentrations in the FGD inlet flue gas were measured to range from 6 to 16  $\mu\text{g}/\text{Nm}^3$ , and elemental mercury concentrations ranged from 3 to nearly 7  $\mu\text{g}/\text{Nm}^3$ . Mercury oxidation percentages averaged 62 to 70%. Manual flue gas sampling by the draft Ontario Hydro method was conducted a few weeks later, and tended to verify the field analyzer results (see below). However, although lower than expected, the measured elemental mercury concentrations were judged to be adequate to support continued catalyst testing at this site.

Several potential reasons were identified as to why the flue gas mercury concentrations were lower than expected. One is that Site 3 fires a wide range of coals. Data from the EPA mercury ICR program show that just over 50% (by tonnage) of the coals fired there contain an average of approximately 0.1 ppm of mercury, while the remainder contain much higher mercury concentrations of 0.3 ppm and greater. The mercury concentrations measured at Site 3 were consistent with firing a fuel blend that is richer in the former, lower mercury content coals, and leaner in the latter. Coal mercury data collected as the project progressed showed that this was an unlikely explanation.

The other potential reason relates to plant operations. The Site 3 boilers are equipped with “low  $\text{NO}_x$ ” burners, and were operating in the low  $\text{NO}_x$  mode, which typically results in relatively high loss-on-ignition (LOI) levels in the fly ash produced, corresponding with high unburned carbon content. Based on previous results with a high LOI ash as a catalyst material, it was speculated that the ash at Site 3 adsorbs and/or oxidizes a portion of the flue gas mercury, and lowers the flue gas mercury concentration relative to the amount of mercury in the coal. Data collected later in the Site 3 test period indicated this to be the primary reason why lower than expected mercury concentrations were measured in the FGD inlet flue gas at Site 3.

Further flue gas and coal characterization efforts were conducted as part of the testing at Site 3. These characterization efforts are discussed later in this section.

### **Short-term Catalyst Screening Test Results**

Regardless of the fact that total mercury concentrations were lower than expected, the measured elemental mercury concentrations of nominally 3 to 6  $\mu\text{g}/\text{Nm}^3$  were determined to be adequate for mercury oxidation catalyst testing. Based on the results of previous laboratory catalyst

screening tests (see Section 4), a number of catalyst materials were selected to be screened in the field at Site 3, as listed below:

**Carbon-based Materials:**

Carbon #1	Carbon #2
Carbon #3	Carbon #4
Carbon #6	

**Fly Ash Materials:**

Subbituminous Ash #4	Subbituminous Ash #5
Bituminous Ash #3	

**Metal-based Catalysts:**

Fe #1	Fe #5
Pd #1	SCR Catalyst

Two screening test sets were completed in June; a third set was completed in July. Metal-based catalysts were evaluated in the first screening test set, which went for approximately 5 days, and the fly ash materials and one of the carbons were evaluated in the second screening test set which lasted 7 days. The third screening test set included all carbon-based catalysts. This set was run for 14 days, because the carbon-based materials are known to have a high mercury adsorption capacity and take longer periods of time to approach adsorption equilibrium.

The results from the three short-term screening tests are summarized in Tables 3-1 and 3-2. Table 3-1 summarizes total mercury adsorption data, while Table 3-2 summarizes elemental mercury oxidation data. In general, at the end of the test the metal catalyst materials in the first screening test set were at or near adsorption equilibrium (observed total mercury breakthrough values were near 100%) and the oxidation percentages were high (approximately 90%). Conversely, the ashes and the one carbon in the second set were still adsorbing appreciable amounts of mercury, and the observed oxidation percentages were relatively low (all less than 50%). After a longer, 14-day duration, the carbons in the third set were approaching adsorption equilibrium, and were observed to achieve relatively high mercury oxidation efficiencies.

Interpretation of the data in Tables 3-1 and 3-2 is confounded by apparent variations in the inlet flue gas total and elemental mercury concentrations during the measurement of catalyst performance. The way the test sequence normally proceeded was for total mercury concentrations throughout the test apparatus to be evaluated one day, and elemental concentrations during the next day. Inlet concentrations for total and/or elemental mercury were measured at the beginning and end of each test day, and the outlet concentrations from each of the six catalyst holders were measured throughout the day. Either the average or an interpolation between the beginning and end of day values was used as the inlet concentration for the “A” position catalysts. For the “B” position catalysts, the outlet of the upstream “A” position catalyst was used as the inlet value. This approach works well when inlet concentrations remain relatively stable throughout the day, but makes data interpretation difficult when inlet concentrations vary significantly.

**Table 3-1**  
**Mercury Adsorption Data from the Short-term Tests at Site 3**

Catalyst Material	Catalyst Position	Bed Inlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Hg Breakthrough (%)
<b>Short-term Test 1</b>				
Pd #1 Bed 1	1A	6.8	6.3	94
Pd #1 Bed 2	1B	6.3	5.2	81
Sand	2A	6.8	5.5	82
SCR Catalyst	2B	5.5	7.2	130
Fe #1	3A	6.8	-	-
Fe #5	3B	-	5.9	87*
<b>Short-term Test 2</b>				
Carbon #4 Bed 1	1A	10.6	5.1	49
Carbon #4 Bed 2	1B	5.1	1.6	31
Sand	2A	12.2	9.1	75
Subbituminous Ash #5	2B	9.1	4.1	45
Subbituminous Ash #4	3A	11.1	6.5	53
Bituminous Ash #3	3B	6.5	3.8	63
<b>Short-term Test 3</b>				
Carbon #1 Bed 1 (2 mg/g)	1A	12.2**	10.5	86**
Carbon #1 Bed 2 (2 mg/g)	1B	10.5	2.1	20
Sand	2A	12.2**	13.2	108**
Carbon #6 (2 mg/g)	2B	13.2	9.0	68
Carbon #3 (2 mg/g)	3A	12.2	10.3	84
Carbon #2 (1 mg/g)	3B	10.3	6.5	63

\*Total for both beds in series.

\*\*These numbers should be considered approximate due to variability in inlet total Hg concentrations over the course of the day.

During the total mercury measurements for short-term Test 1, the total mercury concentrations in the inlet flue gas varied over a wide range, from a morning average of  $12.9 \mu\text{g}/\text{Nm}^3$  to an evening average of  $6.8 \mu\text{g}/\text{Nm}^3$ . For short-term Test 2, the morning and afternoon average inlet values were  $10.0 \mu\text{g}/\text{Nm}^3$  and  $13.3 \mu\text{g}/\text{Nm}^3$ , respectively. The inlet elemental mercury concentrations similarly varied throughout each test day, although over a narrower range. During short-term Test 1, inlet elemental mercury concentrations varied from an average of  $4.5 \mu\text{g}/\text{Nm}^3$  in the morning to  $3.0 \mu\text{g}/\text{Nm}^3$  in the afternoon. For Test 2, the corresponding averages were  $6.1 \mu\text{g}/\text{Nm}^3$  in the morning and  $4.4 \mu\text{g}/\text{Nm}^3$  in the afternoon.

**Table 3-2**  
**Elemental Mercury Oxidation Data from the Short-term Tests at Site 3**

Catalyst Material	Catalyst Position	Bed Inlet Elemental Hg (mg/Nm <sup>3</sup> )	Bed Outlet Elemental Hg (mg/Nm <sup>3</sup> )	Observed Elemental Hg Oxidation (%)
<b>Short-term Test 1</b>				
Pd #1 Bed 1	1A	4.3	0.4	92
Pd #1 Bed 2	1B	-	-	-
Sand	2A	4.0	3.2	19
SCR Catalyst	2B	3.2	0.4	87
Fe #1	3A	4.9	0.5	90
Fe #5	3B	-	-	-
<b>Short-term Test 2</b>				
Carbon #4 Bed 1	1A	5.9	5.5	7
Carbon #4 Bed 2	1B	5.5	4.9	10
Sand	2A	5.6	4.5	19
Subbituminous Ash #5	2B	4.5	2.5	44
Subbituminous Ash #4	3A	5.4	3.4	37
Bituminous Ash #3	3B	3.4	3.8	-11
<b>Short-term Test 3</b>				
Carbon #1 Bed 1 (2 mg/g)	1A	2.6	0.72	73
Carbon #1 Bed 2 (2 mg/g)	1B	0.72	-	-
Sand	2A	2.6	1.8	67
Carbon #6 (2 mg/g)	2B	1.8	0.68	62
Carbon #3 (2 mg/g)	3A	2.6	0.17	93
Carbon #2 (1 mg/g)	3B	0.17	-	-

These observed variations are most likely caused by fluctuations in the coal blend fired at Site 3. As mentioned above, Site 3 fires a broad range of Pennsylvania and West Virginia coals, with widely varying mercury contents reported for each. Also, variations in unit load, excess air levels, and fly ash LOI may impact measured mercury concentrations in the flue gas.

Because of these apparent fluctuations in the inlet mercury concentrations, the inlet concentrations shown in the tables have a potentially large error associated with them. That is, the actual inlet concentration to a particular catalyst bed during the time the outlet concentration was being measured may have been significantly higher or lower than the value shown in the table. The value in the table may have been taken an hour or more earlier or later, or may have been linearly interpolated by time of day between the morning and afternoon values. Over an hour or more of time, the actual inlet concentration may have varied significantly, and the assumption of a linear variation in mercury concentration with time may not be valid.

The observed variations in inlet total and elemental mercury concentrations no doubt contribute to errors in some of the results reported, such as in Table 3-1 where the outlet total mercury concentration from the SCR catalyst bed was higher than the inlet value. However, these errors will not greatly affect the results as to which catalyst materials showed the highest oxidation percentages. High oxidation percentages correspond with very low outlet concentrations (less than  $1 \mu\text{g}/\text{Nm}^3$ ). The calculated oxidation percentages for high activity materials are consequently not very sensitive to the measured inlet value.

It should also be noted that prior to measuring the elemental mercury concentrations for the second short-term test, stannous chloride solution was siphoned from the first impinger in the analytical train back through the heated sample line to the catalyst box. The sample line was connected to the outlet of the 3B catalyst holder (Bituminous Ash #3) at the time. The presence of some stannous chloride at the outlet of this catalyst holder may account for the outlet elemental concentration from this catalyst being higher than the inlet (the inlet concentration value fluctuations discussed above may also account for this apparent error). The heated sample line was flushed and dried after this episode, so the values for the other catalyst beds should not have been affected. The fact that the inlet mercury oxidation percentages measured after this episode match earlier measurements (62 to 70% oxidation) provides further credence that the other values were not affected.

Additionally, note that on the final day of the second short-term test, the measured temperature of catalyst train 2 dropped to  $190^\circ\text{F}$  ( $88^\circ\text{C}$ ) overnight. The reason for this drop was not apparent, although the temperature controller set point was found to be at  $250^\circ\text{F}$  ( $121^\circ\text{C}$ ) rather than  $300^\circ\text{F}$  ( $149^\circ\text{C}$ ). The set point on the controller was raised, and the catalyst train temperature reading was restored to  $300^\circ\text{F}$  ( $149^\circ\text{C}$ ) for several hours before measuring the outlet elemental mercury concentrations from the Subbituminous Ash #5 (position 2B). However, this temperature excursion may have adversely affected the activity of this catalyst material, and may account for the lower than expected activity of the Subbituminous Ash #5 at Site 3.

During initial catalyst performance measurements for short-term Test 3, project team members noted a low bias in elemental mercury concentrations measured upstream of the catalyst beds. The bias was traced to a buildup of fly ash in the filter at the flue gas inlet to the catalyst test unit. Apparently the fly ash loadings at Site 3 at the FGD inlet location are high enough that over a period of two weeks or longer, a great deal of fly ash can collect on the filter upstream of the catalyst beds. Also, it was apparent from the dark color that the ash has a relatively high LOI, and correspondingly was anticipated to have a significant adsorption capacity for elemental mercury. The filter was cleaned and the catalysts were placed back in service. The catalyst performance data reported for short-term Test 3 were collected after the filter was cleaned and the catalysts were put back in service. On all subsequent trips to measure long-term test catalyst activities, this filter was cleaned before any measurements were made.

As mentioned above, mercury concentrations measured at Site 3 tend to vary markedly during the day, most likely due to coal blend changes. This makes measurement of catalyst performance difficult, since the “inlet” mercury concentration value can vary by a factor of two with time. When the inlet total mercury concentrations were measured for short-term Test 3, the concentrations varied from about  $12 \mu\text{g}/\text{Nm}^3$  late in the morning to  $22 \mu\text{g}/\text{Nm}^3$  later that afternoon. Thus, the percent mercury breakthrough values for the first bed of Carbon #1 and for the sand bed should be considered approximate. For the other beds, the upstream concentrations

were measured very close in time to the downstream measurements, so those percent breakthrough values are likely to be more accurate. In general, the upstream carbons in the “A” catalyst holder position were near adsorption equilibrium (>80% mercury breakthrough) while those in the “B” position were still adsorbing appreciable quantities of mercury (20% to 68% mercury breakthrough).

As do the total mercury concentrations, the elemental mercury concentrations in the flue gas at Site 3 appeared to vary during the day, most likely with coal blend variations. Thus, the oxidation percentages for short-term Test 3 should be considered approximate. Carbon #3 was observed to be the most active, but it would be difficult to distinguish between the performance of Carbon #1 and Carbon #2 with these results. It was not possible to measure the performance of Carbon #6, because of the low elemental mercury concentrations remaining in the flue gas downstream of the Carbon #3 bed.

## Long-term Test Results

The screening test results described above were used to identify catalysts for long-term testing at this site. Based on those results, the catalysts listed in Table 3-3 were selected for long-term testing.

**Table 3-3**  
**Catalyst Materials Selected for Testing in the Long-term Test at Site 3**

Catalyst Material	Position	Catalyst Loading	
		(mg per g of sand bed)	(mg total in sand bed)
Pd #1 Bed 1	1A	50	3750
Pd #1 Bed 2	1B	50	3750
Sand blank	2A	-	-
Fe #1	2B	50	3750
Carbon #6	3A	3.33	250
Subbituminous Ash #5	3B	20	1500

The Pd #1 catalyst and the Subbituminous Ash #5 were shown to be active at other sites, particularly Site 2, and thus were chosen for long-term testing at Site 3. The decision to test the Subbituminous Ash #5 was in spite of the fact that it did not show high activity in the results from short-term Test 2. The results of short-term Test 1 showed another metal-based catalyst, Fe #1, was also active in the bituminous coal ash. Since an iron-based catalyst would be much less expensive to produce than a palladium-based catalyst, this material was also selected for long-term testing. Carbon #6 was selected for the long-term test over Carbon #3 based on previous Site 2 results. Carbon #3 was initially highly active at Site 2, but lost activity rapidly over the first few weeks of flue gas exposure. Carbon #6 retained a substantial amount of its original activity over the course of the long-term test at Site 2. Although the mechanisms for catalyst deactivation may be different for Powder River Basin coal versus eastern bituminous coal, it was feared that Carbon #3 would similarly lose activity at Site 3. Thus, it was a judgement call by the project team to select Carbon #6 for the long-term test. Its concentration in the sand bed was



increased from 2 mg/g in the short-term test to 3.33 mg/g in the long-term test to match the concentration tested at Site 2, and to presumably produce a higher mercury oxidation percentage across the bed at Site 3.

The long-term catalyst test was begun on July 13. On July 18, it was discovered that the temperature in the catalyst holder box had dropped to approximately 200°F (93°C) due to failed wiring to some heating elements in the box. The wiring was repaired, and the test was restarted with fresh catalyst materials on July 19. Due to a dwindling supply of the Pd #1 catalyst material, when the test was restarted, bed 1A was charged with only 26.7 mg/g sand of Pd #1 (2000 mg total in the bed) and the second bed was reused from the initial charge. It was thought that the second bed would have been “protected” from any condensing species by the first bed, and therefore should retain high activity.

The early (two-week to one-month) performance of the sand bed catalysts being evaluated in the long-term test would have normally been conducted in early- to mid-August. This testing was delayed because an unplanned host unit outage from August 2 to August 19 caused the catalyst test unit to draw only heated air through the catalyst beds instead of flue gas for that time period. Because the catalysts were purged with air (instead of flue gas) at 300°F (149°C) during this outage, which may have effectively “regenerated” the catalysts, it was decided to wait until at least one month after the outage to conduct initial catalyst performance tests.

The next site visit was carried out during the first week of October 2000. Because of the plant outage August 2<sup>nd</sup> through the 19<sup>th</sup> the October tests represent catalyst results obtained after 8 total weeks of flue gas exposure, including the 2 weeks before the outage, but only 6 weeks of exposure after the plant outage.

Measurements during October characterized the amount of mercury breakthrough across the catalyst beds, and the percent oxidation of elemental mercury across the catalysts. Table 3-4 lists results for mercury adsorption by the catalysts. Adsorption is indicated by the bed outlet total mercury concentration being lower than the inlet concentration.

**Table 3-4**  
**Mercury Adsorption Data from the Long-term Test at Site 3, October 2000**

<b>Catalyst Material</b>	<b>Catalyst Position</b>	<b>Bed Inlet Total Hg (mg/Nm<sup>3</sup>)*</b>	<b>Bed Outlet Total Hg (mg/Nm<sup>3</sup>)**</b>	<b>Observed Hg Breakthrough (%)</b>	<b>Apparent Hg Adsorption (%)</b>
Pd #1 Bed 1	1A	16.3	15.2	93	7
Pd #1 Bed 2	1B	15.2	10.6	70	30
Sand	2A	16.3	15.5	95	5
Fe #1	2B	15.5	14.9	96	4
Carbon #6	3A	16.3	-	-	-
Subbituminous Ash #5	3B	16.3	14.2	82	18

\*Average value based on inlet measurements made during the test period.

\*\*Average based on two series of measurements.

The inlet mercury concentration varied between 14.4 and 18.1 µg/Nm<sup>3</sup> during this measurement period. This variation is less than was observed during the June and July trips. Most of the

catalysts showed very low levels of mercury adsorption. The first bed of Pd #1 showed less than 10% adsorption whereas the second bed appeared to adsorb 30% of the inlet mercury. This suggests that total breakthrough across the second bed had not yet occurred. The Subbituminous Ash #5 removed as much as 20% of the inlet mercury; this sample showed extended mercury adsorption at Site 2.

Adsorption results were not obtained for the Carbon #6, although results obtained with the downstream bed (Subbituminous Ash #5) indicate that removal by the Carbon #6 sample must be less than 18%. Previous results have shown that, in general, the upstream catalysts in the “A” catalyst holder position approach adsorption equilibrium quicker than those in the downstream “B” position.

Table 3-5 lists the results for mercury oxidation across the catalyst beds measured in October. The upstream (“A” position) Pd #1 and Carbon #6 samples showed oxidation percentages above 80%. The latter oxidized nearly all of the mercury. Because of the high oxidation levels measured, and resulting low levels of elemental mercury in the effluent gas, tests were not performed on the beds downstream of these catalysts (the second bed of Pd #1 and Subbituminous Ash #5). Results for the Fe #1 catalyst indicated 57% oxidation of elemental mercury after 8 weeks of flue gas exposure, suggesting that deactivation of this sample may be occurring. In the short-term Test 1 results, this catalyst achieved 90% oxidation.

**Table 3-5**  
**Elemental Mercury Oxidation Data from the Long-term Test at Site 3, October 2000**

<b>Catalyst Material</b>	<b>Catalyst Position</b>	<b>Bed Inlet Elemental Hg (mg/Nm<sup>3</sup>)*</b>	<b>Bed Outlet Elemental Hg (mg/Nm<sup>3</sup>)</b>	<b>Observed Elemental Hg Oxidation (%)</b>
Pd #1 Bed 1	1A	1.81	0.30	83
Pd #1 Bed 2	1B	0.30	**	**
Sand	2A	1.81	1.78	1.4
Fe #1	2B	1.78	0.77	57
Carbon #6	3A	1.81	0.05	97
Subbituminous Ash #5	3B	0.05	**	**

\* Average value based on inlet measurements made during the test period.

\*\* Downstream fixed bed concentration not measured due to high oxidation across upstream bed.

The next site visit was carried out during the third week of November. The November tests represent catalyst results obtained after 14 total weeks of flue gas exposure, including the 2 weeks before the outage, but only 12 weeks of exposure after the plant outage. Table 3-6 lists results for mercury adsorption by the catalysts measured during the November trip. The inlet mercury concentration varied between approximately 14 and 20 µg/Nm<sup>3</sup> during this measurement period. This variation is less than was observed during trips in June and July, but consistent with the October results.

Most of the catalysts showed low levels of mercury adsorption. The outlet of the first bed of Pd #1 was not measured; in October it showed less than 10% adsorption. The second bed appeared to adsorb 25% of the inlet mercury. The other beds showed less than 20% mercury

**Table 3-6**  
**Mercury Adsorption Data from the Long-term Test at Site 3, November 2000**

Catalyst Material	Catalyst Position	Bed Inlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Hg Breakthrough (%)	Apparent Hg Adsorption (%)
Pd #1 Bed 1	1A	16.2	-	*	*
Pd #1 Bed 2	1B	16.2	12.2	75	25
Sand	2A	16.2	14.0	86	14
Fe #1	2B	14.0	11.3	81	19
Carbon #6	3A	17.0	14.2	84	16
Subbituminous Ash #5	3B	14.2	12.3	87	13

\* Not measured because of high observed Hg breakthrough at 8 weeks, and because of high observed Hg breakthrough in current tests on the downstream bed. The assumed value is at or near 100%.

adsorption. These results suggest that total breakthrough across these beds had not yet occurred, although several were approaching that point.

Table 3-7 lists the results for mercury oxidation across the catalyst beds as measured in November. The upstream (“A” position) Pd #1 and Carbon #6 samples showed oxidation percentages of 85% or more of the elemental mercury. Both of these percentages are corrected for the observed elemental mercury adsorption and/or oxidation across the sand bed “blank” in the 2A position. Because of the high oxidation levels measured and subsequent low levels of elemental mercury in the effluent gas from the Pd #1 and Carbon #6 catalysts, tests were not performed on their downstream beds (“B” positions). Results for the Fe #1 catalyst indicated 45% oxidation after 14 weeks versus 57% oxidation after 8 weeks of flue gas exposure. This indicates that deactivation of this sample was continuing to occur.

**Table 3-7**  
**Elemental Mercury Oxidation Data from the Long-term Test at Site 3, November 2000**

Catalyst Material	Catalyst Position	Bed Inlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Elemental Hg Oxidation (%)
Pd #1 Bed 1	1A	0.73*	0.10	87*
Pd #1 Bed 2	1B	0.10	**	**
Sand	2A	1.15	0.73	36
Fe #1	2B	0.73	0.41	45
Carbon #6	3A	0.73*	0.11	85*
Subbituminous Ash #5	3B	0.11	**	**

\*These values are corrected to account for the observed reduction in elemental mercury concentration across the sand “blank” in position 2A.

\*\*Downstream fixed bed concentration not measured due to high oxidation across upstream bed.

The next site visit was carried out the week of December 18. The December results represent catalyst performance after 19 total weeks of flue gas exposure, including the 2 weeks before the outage, but 17 weeks of exposure after the plant outage.

Table 3-8 lists results for mercury adsorption by the catalysts as measured in December. Individual inlet mercury concentration measurements were observed to vary from approximately 10 to greater than 25  $\mu\text{g}/\text{Nm}^3$  during this measurement period. This variation is somewhat greater than was observed during the previous trips. However, during most of the measurement period, the inlet values varied over a narrower range of approximately 10 to 14  $\mu\text{g}/\text{Nm}^3$ , which is more consistent with October and November results.

**Table 3-8**  
**Mercury Adsorption Data from the Long-term Test at Site 3, December 2000**

Catalyst Material	Catalyst Position	Bed Inlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Hg Breakthrough (%)	Apparent Hg Adsorption (%)
Pd #1 Bed 1	1A	17.0	14.3*	*	*
Pd #1 Bed 2	1B	14.3*	13.3*	*	*
Sand	2A	10.8	9.4	87	13
Fe #1	2B	9.4	10.3	100	0
Carbon #6	3A	10.8	10.2	95	5
Subbituminous Ash #5	3B	10.2	8.3	81	19

\*These numbers are most likely invalid because of plugged flow downstream of the “1” catalyst train – sample gas was most likely the only gas flow across this catalyst train, and only during sampling.

Most of the catalysts showed low levels of mercury adsorption. However, the gas path for the two beds of Pd #1 appeared to be plugged downstream of the catalyst beds but upstream of the sample pump. The flow meter for this gas path indicated no gas flow. Therefore, valid results could not be measured for these beds. The other beds showed less than 20% mercury adsorption. The results suggest that total breakthrough had not yet occurred across the sand blank, Carbon #6, and Subbituminous Ash #5 beds, but that breakthrough had occurred across the Fe #1 bed. However, with the fluctuation in inlet mercury loading observed in the Site 3 flue gas during this measurement period, it would be difficult to quantify breakthrough to greater accuracy than about plus or minus 20%. A bed inlet mercury concentration could easily vary by this amount while the outlet concentration was being measured. Consequently, it is not possible to report with certainty which beds had achieved adsorption equilibrium and which had not.

Table 3-9 lists the results for mercury oxidation across the catalyst beds from December 2000. The results in the table are difficult to interpret because of several confounding effects:

- As mentioned above, the gas flow through the Pd #1 catalyst sample beds appeared to be plugged, making the results from measurements on the outlet gas from these beds invalid;
- The inlet sample elemental mercury concentrations were very low ( $<1 \mu\text{g}/\text{Nm}^3$ ), approaching the detection limit for the field mercury analyzer, which makes measurement of catalyst outlet concentrations difficult;

**Table 3-9**  
**Elemental Mercury Oxidation Data from the Long-term Test at Site 3, December 2000**

Catalyst Material	Catalyst Position	Bed Inlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Elemental Hg Oxidation (%)
Pd #1 Bed 1	1A	0.36*	0.39**	**
Pd #1 Bed 2	1B	0.39**	0.45**	**
Sand	2A	0.86	0.36	58
Fe #1	2B	0.36	ND	-
Carbon #6	3A	0.36*	~0.0	-
Subbituminous Ash #5	3B	~0.0	~0.0	-

\*These values are corrected to account for the observed reduction in elemental mercury concentration across the sand “blank” in position 2A.

\*\*These numbers are most likely invalid because of plugged flow downstream of the “1” catalyst train – sample gas was most likely the only gas flow across this catalyst train, and only during sampling.

ND – Not determined due to high noise levels in the analyzer output.

- The field mercury analyzer output was relatively noisy during this sampling period, for reasons unknown, making it more difficult than normal to accurately measure elemental mercury concentrations below  $1 \mu\text{g}/\text{Nm}^3$ ; and
- The sand blank bed in position 2A appeared to adsorb and/or oxidize a relatively high percentage of the already low inlet elemental mercury content, making the adjusted inlet elemental mercury concentrations to the other beds even lower.

Based on the limited results in Table 3-9, it appears that Carbon #6 might still be achieving relatively high elemental mercury oxidation (the value was 85% in November), but the December data were otherwise not of high enough quality to quantify the performance of the catalysts.

The low inlet elemental mercury concentration of about  $0.9 \mu\text{g}/\text{Nm}^3$  shown in Table 3-9 corresponds with a very high mercury oxidation percentage of 94% that day. This was a much higher oxidation percentage than was observed during the initial testing at Site 3 in June 2000 (62 to 70%).

The last site visit at Site 3 was carried out the weeks of January 22 and January 29, 2001. Testing at Site 3 was concluded at the end of this test period. The January measurements represent catalyst results obtained after 27 to 28 total weeks of flue gas exposure, including the 2 weeks before the outage, but only about 23 weeks of exposure after the plant outage.

Table 3-10 lists results for mercury adsorption by the catalysts as measured in January. Individual inlet mercury concentration measurements were observed to vary from less than 1 to greater than  $20 \mu\text{g}/\text{Nm}^3$  during this measurement period. This is the widest variation seen during sampling at Site 3, and appears to be related to wide variations in the coal quality. During part of the trip, the plant was firing coal from the coal pile, while other periods they were firing coal from trains and from truckload shipments. However, during most of the mercury breakthrough

**Table 3-10**  
**Mercury Adsorption Data from the Long-term Test at Site 3, January 2001**

Catalyst Material	Catalyst Position	Bed Inlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Bed Outlet Total Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Hg Breakthrough (%)	Apparent Hg Adsorption (%)
Pd #1 Bed 1	1A	9.4	9.9	*	*
Pd #1 Bed 2	1B	9.9	7.7	*	*
Sand	2A	9.9	8.1	82	18
Fe #1	2B	8.1	6.7	83	17
Carbon #6	3A	11.5	7.0	61	39
Carbon #6 repeat	3A	8.4	7.5	89	11
Subbituminous Ash #5	3B	7.0	4.4	63	37
Subbituminous Ash #5 repeat	3B	7.5	5.8	78	22

\*These numbers were not calculated because of plugged flow downstream of the “1” catalyst train – gas flow to the analyzer was the only flow across these beds, so may not be indicative of catalyst performance.

measurement period the inlet values varied over a narrower range of approximately 8 to 13  $\mu\text{g}/\text{Nm}^3$ , which is more consistent with previous results.

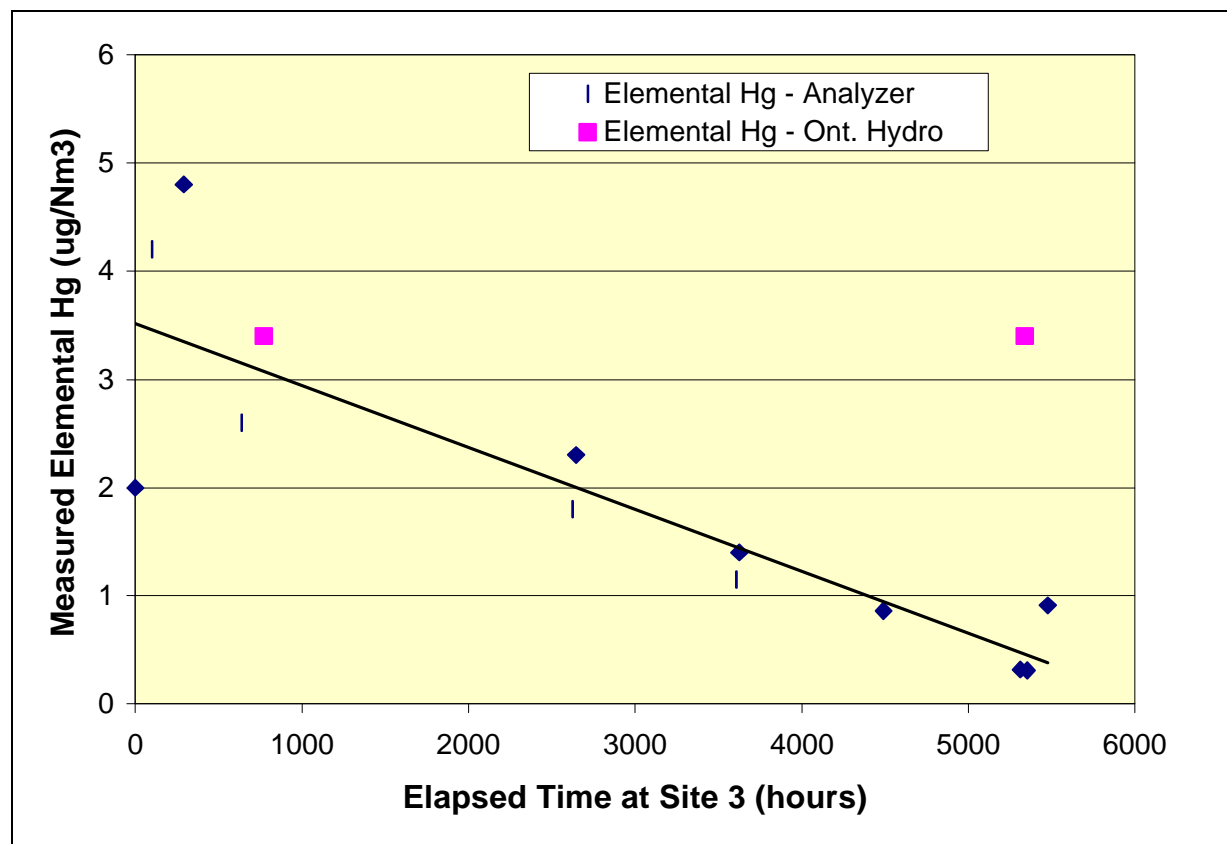
Most of the catalysts showed low levels of mercury adsorption. However, the gas path for the two beds of Pd #1 was observed to be plugged at the flow measurement orifice, which is downstream of the catalyst beds but upstream of the sample pump, as it had been during the December trip. Therefore, valid results could not be measured for these beds. The other beds showed 11% to 39% mercury adsorption. As mentioned above, with the fluctuation in inlet mercury loading observed in the Site 3 flue gas, it was difficult to quantify breakthrough to greater accuracy than about plus or minus 20%. A bed inlet mercury concentration could easily vary by this amount while the outlet concentration was being measured. Consequently, it is not possible to determine which beds had achieved adsorption equilibrium and which had not. Also, with the low inlet total mercury concentrations measured at times during this measurement trip, it is possible that the beds desorbed some mercury to low-mercury-content flue gas previously treated and were re-adsorbing mercury when these measurements were being made. There is some evidence of this in that Carbon #6 and Subbituminous Ash #5 samples were measured for adsorption a second time during this test period, and showed lower adsorption percentages than in the first measurements.

No results were measured in January for mercury oxidation across the catalyst beds, for several reasons. These reasons were similar to those that impacted the December measurements:

- The gas flow through the Pd #1 catalyst sample beds was plugged in the downstream flow measurement orifice, making the results from measurements on the outlet gas from these beds invalid;
- The inlet sample elemental mercury concentrations were very low (0.1 to 0.9  $\mu\text{g}/\text{Nm}^3$ ), approaching the detection limit for the field mercury analyzer, which made measurement of catalyst outlet concentrations difficult; and

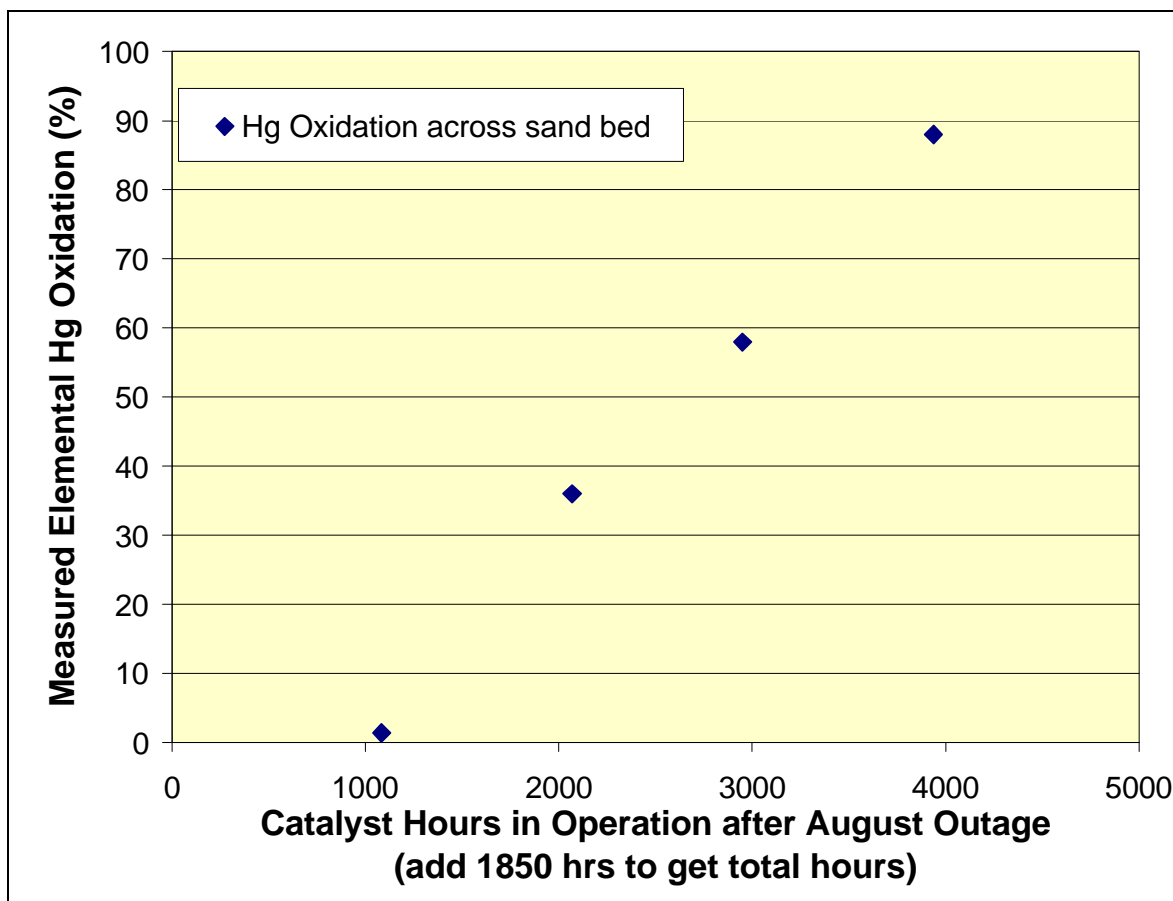
- The sand blank bed in position 2A appeared to adsorb and/or oxidize a relatively high percentage of the already low inlet elemental mercury content, making the adjusted inlet elemental mercury concentrations to the other beds essentially zero. A sand bed outlet concentration of  $0.1 \mu\text{g}/\text{Nm}^3$  was measured immediately after the bed inlet concentration had been measured at  $0.9 \mu\text{g}/\text{Nm}^3$ .

Consequently, there are no end-of-test mercury oxidation results to report. In retrospect, the ability to measure catalyst mercury oxidation performance at Site 3 were confounded by two ongoing effects that become apparent when reviewing and analyzing the performance data tabulated above. First, the elemental mercury concentrations measured with the field analyzer at the inlet to the long-term test apparatus were observed to decrease almost linearly over time. This effect is illustrated in Figure 3-2. Note, however, that the elemental mercury concentrations measured by the draft Ontario Hydro method at the beginning and end of the long-term test period do not show a similar downward trend; the same value of 3 to  $4 \mu\text{g}/\text{Nm}^3$  was measured both times.



**Figure 3-2**  
**Observed Decrease in Measured Elemental Mercury Concentrations over Time at Site 3**

Second, the apparent oxidation percentage across the sand bed blank was observed to increase over time. This effect is illustrated in Figure 3-3. The net of these two effects is that there have not been sufficient elemental mercury concentrations measured at the long-term test apparatus to measure catalyst performance at Site 3 since the November measurement trip.

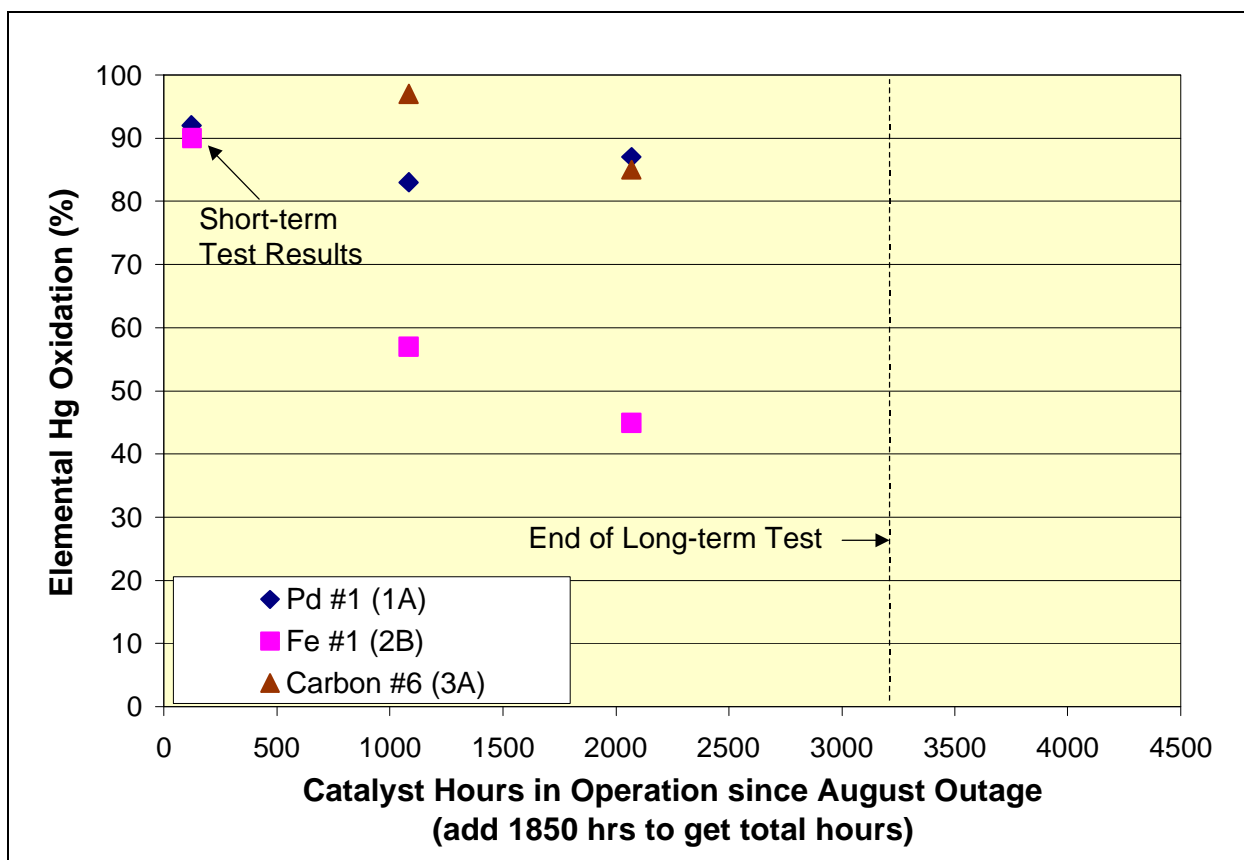


**Figure 3-3**  
**Apparent Elemental Mercury Oxidation Percentage vs. Time in Operation for the Sand Bed Blank in the Long-term Test Apparatus**

Figure 3-4 illustrates the catalyst oxidation results available from the long-term test at Site 3, which are limited to short-term test data and results measured in October and November. The results plotted in Figure 3-4 show that the upstream Pd #1 catalyst and the Carbon #6 remained active (greater than 80% oxidation of elemental mercury) through approximately 2100 hours since the August outage was over (almost 4000 hours since the long-term test began). The Fe #1 catalyst had begun to lose activity (less than 50% oxidation of elemental mercury). No results are available for the downstream bed of Pd #1 or for the Subbituminous Ash #5, because those beds were downstream of beds that remained at high oxidation activity through at least November. The catalyst bed materials were recovered at the end of the test, and laboratory tests were conducted to measure end-of-test catalyst performance in a simulated flue gas (see Section 4).

No reason has been identified as to why the elemental mercury concentrations measured by the field analyzer in December and January were too low to allow evaluation of catalyst performance, in spite of the fact that in January sampling by the Ontario Hydro method showed much higher elemental mercury concentrations. Quality control measures employed to improve analyzer performance included:





**Figure 3-4**  
**Long-term Catalyst Oxidation Results from Site 3**

- Replacing the quartz probe liner in the flue gas duct;
- Replacing Teflon<sup>®</sup> sample lines;
- Ensuring that all sample lines were adequately heat traced and that no moisture was condensed in the lines;
- Cleaning all fly ash from the filter in the long-term test apparatus upstream of the catalyst beds;
- Cleaning and/or replacing impingers in the analyzer sampling train;
- Replacing impinger solutions;
- Replacing the gold in the adsorption portion of the analyzer; and
- Recalibrating the analyzer with an elemental mercury standard.

None of these efforts were found to measurably affect the elemental mercury concentrations measured by the field analyzer at the FGD inlet location. As all quality control checks verified proper performance of the mercury analyzer, it is believed that the apparent long-term change in measured elemental mercury at the FGD inlet location was caused by mercury absorption within the long-term test apparatus or sample delivery system, possibly involving reactions with fly ash.

## Commercial Catalyst Form Tests

A long-term honeycomb catalyst test also started in July 2000. The objective of the test was to collect data regarding the performance of catalyst materials applied to commercially available structures in Site 3 bituminous coal flue gas conditions. In these tests, two 2-inch (51-mm) lengths of Pd #1 catalyst (30 g/ft<sup>3</sup> or 850 mg/m<sup>3</sup> loading) in series were placed in service in a separate 300°F (149°C) hot box, installed at the FGD inlet location beside the long-term sand bed test apparatus. This second hot box was set up to pull a flue gas sample through a separate probe from that for the long-term sand bed apparatus. The honeycomb samples were prepared at three times the palladium loading tested at Site 2, based on laboratory results that showed the higher loading being required to ensure high activity of the wash-coated honeycomb catalyst.

The alumina honeycomb substrate was similar in pitch to catalysts used for “cold-side” SCR applications (i.e., in applications with low particulate loadings remaining in the flue gas). The honeycomb has a cell density of 64 cpsi, a 3.2-mm pitch, and a geometric surface area of about 340 ft<sup>2</sup>/ft<sup>3</sup> (1100 m<sup>2</sup>/m<sup>3</sup>).

Evaluation of the honeycomb samples was not possible during the first return sampling trip to Site 3, in October 2000, due to an equipment problem. The heater servicing the second hot box failed due to corrosion of a wire. Additional parts needed to correct the problem were not available on site, so the apparatus was shut down. The honeycomb sample hot box was repaired during the next site visit in November and the honeycomb catalyst test was restarted at that time. Because the hot box had been at low temperature for some time, presumably allowing condensable species in the flue gas to foul the catalyst surface, the honeycomb catalyst test was restarted with fresh honeycomb samples after the hot box was repaired. Initial catalyst performance measurements were made the next day. Table 3-11 summarizes the mercury adsorption data for these samples, and Table 3-12 summarizes the elemental mercury oxidation data.

**Table 3-11**  
**November Mercury Adsorption Data from the Honeycomb Sample Test at Site 3**

Catalyst Material	Honeycomb Catalyst Position	Inlet Total Hg (mg/Nm <sup>3</sup> )	Outlet Total Hg (mg/Nm <sup>3</sup> )	Observed Hg Breakthrough (%)	Apparent Hg Adsorption (%)
Pd #1 Honeycomb Sample 1	1A	14.6	11.9	81*	19*
Pd #1 Honeycomb Sample 2	1B	11.9	16.2	136*	0*

\*Since the outlet concentration from the second honeycomb was measured to be higher than the inlet of the first honeycomb in series, this is taken as evidence of inlet mercury variation, and that both samples are essentially at adsorption equilibrium.

The mercury adsorption data in Table 3-11 suggest that both honeycomb samples were at adsorption equilibrium. The outlet total mercury concentration from the second honeycomb sample in series was greater than the concentrations measured at the inlet or the outlet of the upstream sample, but within the range of total mercury concentrations measured for the Site 3 flue gas during this trip. This suggests that the concentrations measured at all three locations

**Table 3-12**

### November Elemental Mercury Oxidation Data from the Honeycomb Sample Test at Site 3

Catalyst Material	Honeycomb Catalyst Position	Approx. Area Velocity (sft/hr)*	Inlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Outlet Elemental Hg ( $\mu\text{g}/\text{Nm}^3$ )	Observed Elemental Hg Oxidation (%)
Pd #1 Honeycomb Sample 1	1A	170	1.40	0.42	70
Pd #1 Honeycomb Sample 2	1B	170	0.42	0.33	21**
Two Beds in Series	-	86	1.40	0.33	76

\*170 sft/hr is equivalent to 50 Nm/hr; 86 sft/hr is equivalent to 25 Nm/hr.

\*\*Both the inlet and outlet concentrations for this sample are near the detection limit for the field analyzer; the observed percent oxidation of elemental mercury across this sample may not be a meaningful value.

represent little or no mercury adsorption, only normal mercury concentration fluctuations in the inlet flue gas.

The elemental mercury oxidation data in Table 3-12 show that the honeycomb samples were active. However, the low inlet elemental mercury concentrations observed make it difficult to quantify the oxidation percentages being achieved. Particularly for the second honeycomb in series, the very low inlet elemental concentration of less than  $0.5 \mu\text{g}/\text{Nm}^3$  is near the detection limit of the analyzer, so the percent reduction value shown in the table is of questionable accuracy.

The observed 70% oxidation for the first honeycomb compares well with a conversion of 80% predicted using a previously developed mass transfer model that assumes instantaneous oxidation when mercury contacts the honeycomb surface. The effective area velocities for these catalysts are approximately 170 standard ft/hr (50 Nm/hr) for each sample individually, and 86 standard ft/hr (25 Nm/hr) for the two in series. Note that at Site 2, the Pd #1 honeycomb achieved only 51% oxidation at a similar area velocity of 190 standard ft/hr (56 Nm/hr) with one 2-inch (51-mm) honeycomb length, and 56% at an area velocity of 105 standard ft/hr (30 Nm/hr) with two 2-inch (51-mm) lengths in series. These results from Site 3 indicate that increasing the palladium loading by a factor of three over the loading tested at Site 2 was effective at improving honeycomb mercury oxidation performance.

The honeycomb catalyst was left in service after the November measurement trip, with the objective of measuring the change in performance with time during subsequent sampling trips. However, more problems were encountered with the honeycomb catalyst test apparatus during the December trip. Electrical problems had allowed the probe and catalyst hot boxes to cool, and both a flue gas leak and a cold spot with resulting moisture condensation were found in the heat-traced sample line from the probe box to the catalyst holder. These problems were repaired and the honeycomb catalysts were left in service once again. No performance data were collected for the honeycomb catalysts, though, because of the low elemental mercury concentrations measured by the field analyzer, as mentioned above in the discussion of the long-term sand bed test results.

It should be noted that the honeycomb catalyst test apparatus was a relatively makeshift device, and did not contain the level of instrumentation and automation found in the sand bed long-term test apparatus. While the makeshift honeycomb test apparatus had operated in a relatively

reliable fashion at Site 2, the higher sulfur content of the flue gas at Site 3 apparently caused more component failures there.

Additional tests were planned in January with the Pd #1 catalyst on a honeycomb structure, to further evaluate the effects of area velocity and catalyst loading on mercury oxidation. The objective of these tests was to determine optimal operating parameters for the honeycomb catalyst. However, due to the extremely low elemental mercury concentrations measured with the field analyzer in the flue gas entering the honeycomb catalyst test apparatus, it was not possible to evaluate catalyst performance during the January trip.

There was concern that the low elemental mercury concentrations measured might be due to fly ash buildup on the quartz-lined probes used to pull flue gas from the scrubber inlet duct to the two test apparatus (long-term and honeycomb configurations). However, the quartz liner on the probe used to withdraw flue gas for the honeycomb catalyst test apparatus was replaced with a new liner, and elemental mercury concentrations measured on gas pulled through the new probe liner remained below  $1 \mu\text{g}/\text{Nm}^3$ . Consequently, the short-term honeycomb test results from November, as reported in Tables 3-11 and 3-12, are the only honeycomb results available from Site 3.

## **Flue Gas Characterization Results**

Flue gas characterization measurements were made at Site 3 at the beginning of the long-term sand bed catalyst test, the week of July 17-21, and at the end, during the last two weeks of January 2001. The July measurements included measurement of speciated mercury concentrations by the draft Ontario Hydro method, mercury and total metals by Method 29, flue gas HCl, chlorine and HF concentrations by Method 26a, and sulfuric acid concentrations by the Controlled Condensation System (CCS) method. Coal and fly ash samples were also collected during the flue gas testing.

Because test results with the field mercury analyzer used in concert with the long-term catalyst test indicated an appreciable drop in elemental mercury content in the FGD inlet gas since the beginning of the long-term test in July, it was decided to conduct more gas characterization tests. These gas characterization tests, conducted in January 2001, included total mercury and mercury speciation by the draft Ontario Hydro method, at FGD inlet and outlet locations and at the Site 3 air heater inlet and outlet. Figure 3-5 illustrates all of the sampling locations. The sampling at the air heater outlet location was conducted with the plant's ammonia injection system turned off, as the presence of ammonia in the flue gas would interfere with the measurement method. While measuring at the FGD inlet location with the ammonia injection system in normal operation, ammonia slip measurements were also conducted. Coal and fly ash samples were also collected intermittently during flue gas testing.

Also in January, flue gas sulfuric acid concentrations were measured at all four locations mentioned above, using the CCS method. The air heater inlet and outlet locations were sampled simultaneously on one day, and the FGD inlet and outlet locations were sampled simultaneously on another day. As were the Ontario Hydro method measurements, the CCS measurements at the air heater inlet and outlet were made with the plant ammonia conditioning system turned off, while the FGD inlet and outlet measurements were made with the ammonia conditioning system in normal operation.

Finally, during the January trip a second mercury SCCEM was operated in conjunction with the analyzer setup at the FGD inlet. The second SCCEM was moved several times during the two-week test period, and used to measure flue gas mercury concentrations at the FGD outlet, air heater inlet, and air heater outlet locations.

The following presents and discusses the flue gas characterization data from Site 3, collected during July 2000 and January 2001.

### **Flue Gas Mercury Concentrations**

Table 3-13 summarizes the July results from the Ontario Hydro method for total and speciated mercury concentrations in the flue gas at the FGD inlet and outlet. The Ontario Hydro method for determining the mercury speciation involves analyzing the oxidized and elemental mercury captured in an impinger train containing solutions of potassium chloride (KCl), potassium permanganate (KMnO<sub>4</sub>), and peroxide (H<sub>2</sub>O<sub>2</sub>). FGD inlet and outlet measurements were taken simultaneously to compare the amount of elemental mercury in each stream. An apparent leak during the third sampling run at the FGD inlet prevented those results from being used.

**Table 3-13**  
**Results of Ontario Hydro Mercury Measurements at Site 3, July 2000**

<b>Sample</b>	<b>Oxidized Mercury (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>Elemental Mercury (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>Total Mercury (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>Mercury Oxidation (%)</b>
Inlet-1	9.2	2.5	11.8	78
Inlet-2	9.6	4.3	13.9	69
Inlet-3*	6.0	0.2	6.1	97
Average	9.4	3.4	12.8	74
Outlet-1	0.58	0.56	1.14	51
Outlet-2	0.71	0.21	0.92	77
Outlet-3	0.24	0.19	0.43	55
Average	0.51	0.32	0.83	61

\*Apparent leak during sampling, not included in average

The results from the first two runs at the FGD inlet show total mercury concentrations of about 13  $\mu\text{g}/\text{Nm}^3$ . The mercury oxidation averaged about 74%, producing elemental mercury concentrations of about 3.4  $\mu\text{g}/\text{Nm}^3$ . These concentrations and oxidation percentage are consistent with measurements made in June and July 2000 with the EPRI semi-continuous field mercury analyzer at this location.

The results in Table 3-13 also indicate 95% removal of oxidized mercury across the FGD absorber, and over 90% removal of elemental mercury. The oxidized mercury removal percentage is consistent with results from other sites, but the high elemental mercury removal percentage is very much unexpected. Experience at the other two sites in this project and results from the EPA mercury ICR for systems with wet FGD led us to expect no removal of elemental mercury across the FGD system; an outlet elemental mercury concentration of 3 to 4  $\mu\text{g}/\text{Nm}^3$

was therefore expected. It is possible that the high apparent removal is due to an analytical problem with the outlet impinger solutions, leading to low recovery of mercury in the downstream (elemental mercury) impingers. However, we cannot point to a specific analytical problem that explains this result.

Table 3-14 shows the results of the EPA Method 29 total mercury concentrations at the FGD inlet location. Method 29 sampling was not conducted at the FGD outlet location. Method 29 results represent a sum of recovered mercury from several sample train impingers and a probe rinse, and indicate only a total (not speciated) mercury concentration. Runs 2 and 3 show concentrations of about 13 to 14  $\mu\text{g}/\text{Nm}^3$  that are very similar to the total mercury concentrations in the first two Ontario Hydro runs. A much higher concentration of 21  $\mu\text{g}/\text{Nm}^3$  was indicated for Run 1, but even this higher value was in the range of individual measurements previously made with the EPRI semi-continuous field mercury analyzer at this location.

**Table 3-14**  
**Method 29 Mercury Results for the FGD Inlet Location**

Run Number	Total Mercury Concentration ( $\mu\text{g}/\text{Nm}^3$ )
1	21.0
2	13.9
3	13.9
Average	16.3

Ontario Hydro method measurements were conducted again at the end of the long-term sand-bed reactor test at Site 3, in January 2001. FGD inlet and outlet Ontario Hydro results were conducted while the ammonia conditioning system was in service at the ESP inlet. Ammonia slip measurements were also made during the sampling effort; these results are not presented, as the measured values at the FGD inlet were all less than 0.2 ppm (the method detection limit). Ontario Hydro measurements were also made at the Site 3 air heater inlet and outlet. These measurements were made with the ammonia conditioning system out of service, as it was expected that the presence of ammonia in the sample gas would interfere with the Ontario Hydro method. The results of the Ontario Hydro measurements in January 2001 are summarized in Table 3-15.

The results in Table 3-15 for the Ontario Hydro method testing at the FGD inlet and outlet locations show much higher elemental mercury concentrations than were measured with the field analyzer at either location. An average of 3.4  $\mu\text{g}/\text{Nm}^3$  was measured at the FGD inlet and 4.5  $\mu\text{g}/\text{Nm}^3$  at the FGD outlet, while the mercury field analyzer typically measured less than 1  $\mu\text{g}/\text{Nm}^3$  at the FGD inlet location and a second analyzer measured less than 3  $\mu\text{g}/\text{Nm}^3$  at the FGD outlet. There is no ready explanation for this discrepancy. The low elemental mercury concentrations were measured with two separate analyzers at the two locations. As discussed above, in July 2000, the field analyzer at the FGD inlet location was observed to be in good agreement with Ontario Hydro measurements. As described earlier in this section, a number of

**Table 3-15**  
**Ontario Hydro Method Results from Site 3, January 2001**

<b>Date/Time</b>	<b>Location</b>	<b>Elemental Hg (ug/Nm<sup>3</sup>)</b>	<b>Oxidized Hg (ug/Nm<sup>3</sup>)</b>	<b>Total Hg (ug/Nm<sup>3</sup>)</b>	<b>Measured Hg Oxidation (%)</b>
1/26/01 13:30	AH Inlet	7.1	37.1	44.2	84.0
1/26/01 15:30	AH Inlet	4.5	30.6	35.1	87.2
1/26/01 19:30	AH Inlet	5.1	28.7	33.8	84.8
<b>Average</b>		<b>5.6</b>	<b>32.1</b>	<b>37.7</b>	<b>85.2</b>
1/26/01 14:00	AH Outlet	9.9	27.3	37.2	73.4
1/26/01 16:00	AH Outlet	7.5	18.6	26.1	71.3
1/26/01 19:30	AH Outlet	12.7	15.3	28.0	54.6
<b>Average</b>		<b>10.0</b>	<b>20.4</b>	<b>30.4</b>	<b>67.0</b>
1/24/01 18:20	FGD Inlet	3.3	5.0	8.3	60.0
1/24/01 20:30	FGD Inlet	3.4	4.2	7.6	55.4
<b>Average</b>		<b>3.4</b>	<b>4.6</b>	<b>8.0</b>	<b>57.8</b>
1/24/01 17:30	FGD Outlet	3.95	0.6	4.6	13.4
1/24/01 20:00	FGD Outlet	5.03	0.6	5.6	9.9
<b>Average</b>		<b>4.5</b>	<b>0.6</b>	<b>5.1</b>	<b>11.5</b>

quality control measures were implemented on the field analyzer at the FGD inlet location in January, and no problems were identified.

The Ontario Hydro results from January show about 87% removal of oxidized mercury across the FGD system, but also a small increase in elemental mercury concentration across the FGD system. Both of these results are consistent with Ontario Hydro method data collected at other coal-fired sites equipped with wet FGD systems. However, we might have expected higher oxidized mercury removal percentages at this site, because the FGD absorber operates at a high liquid-to-gas ratio of about 125 gpm/kacfm, and was designed to operate at 95% SO<sub>2</sub> removal efficiency. The removal of oxidized mercury measured across the FGD absorber at Site 3 by the Ontario Hydro method in July was higher than the January result, at 95%. However, the July results also showed 90% removal of elemental mercury across the absorber, which was not expected, while the January data showed a more expected small increase in elemental mercury concentration across the absorber.

There are several things to note about the air heater inlet and outlet results summarized in Table 3-15. First, the Ontario Hydro method results show the relatively high flue gas mercury concentrations expected based on the EPA mercury ICR coal data for this site. The ICR data showed that the Site 3 coal averaged about 0.25 ppm total mercury content, with some coal samples containing as much as 0.50 ppm. Based on the coal data, we expected to routinely see flue gas total mercury concentrations of 25 µg/Nm<sup>3</sup> and greater, but normally saw average values of only 10 to 15 µg/Nm<sup>3</sup> at the FGD inlet location. The results in Table 3-15 show that flue gas

mercury concentrations are much higher at the air heater inlet location, where the flue gas temperature is about 700°F (370°C). The concentrations decrease across the air heater and ESP as the flue gas temperature drops to 300°F (149°C) and residence time is available for mercury adsorption on fly ash. The apparent mercury adsorption across the air heater amounts to about 19% of the inlet mercury, and that across the ESP and air heater together (i.e., at the FGD inlet) amounts to as much as 79% of the air heater inlet value. However, the FGD inlet sampling was done on a previous day, and the coal mercury content on that day was measured to be slightly lower. Given the small differences in coal sample mercury content for these two days, the apparent removal percentage may be overstated by one or two percentage points.

It is not clear what, if any, role ammonia might play in the adsorption of mercury on the fly ash. The mercury concentrations in the air heater inlet and outlet were measured with the ammonia injection system turned off, while the FGD inlet and outlet values were measured with the ammonia injection system operating. The effects of ammonia injection could, in part, account for the significant observed mercury removal across the ESP (approximately 60% of the air heater inlet mercury concentration). Fly ash samples collected during ammonia injection and subsequently while the ammonia injection system was turned off suggest a possible effect (see further discussions below).

Another thing to note about these data is that the elemental mercury concentration in the flue gas appears to increase across the air heater. This is not an expected result. The concentration of elemental mercury would be expected to decrease across the air heater due to two effects: 1) adsorption on fly ash and 2) oxidation on fly ash surfaces and/or through gas phase reactions with HCl. We do not have a ready explanation for this result; it may represent sampling and/or analytical bias.

Overall, from the air heater inlet to the FGD system outlet, the data in Table 3-15 indicate 86% mercury removal, assuming that virtually all of the mercury in the coal is in the flue gas at the air heater inlet location. These Ontario Hydro speciation data show 98% removal of oxidized mercury from the air heater inlet to the FGD outlet, but only 20% removal of elemental mercury. These percentages underscore the potential effectiveness of a mercury oxidation catalyst installed at the FGD inlet location in improving overall mercury capture.

### ***Other Metals in the Flue Gas***

During the July 2000 gas characterization effort at Site 3, Method 29 was employed to measure the concentrations of other metals (besides mercury) in the flue gas at the FGD inlet location. As a result of there being a relatively high ash content in the flue gas downstream of the ESP at Site 3, the EPA Method 29 sampling results for other metals are being reported as either solid phase metals or gas phase metals. Solid phase metals include the ash collected on the sample train filters and the probe nozzle rinse, while gas phase metals are those collected in the impingers during the sampling runs. The gas phase results indicate species that could absorb from the flue gas onto the catalyst materials and/or participate in catalyst deactivation. However, because the Site 3 flue gas contains a relatively high concentration of fly ash at the FGD inlet location, solid phase metals could be important because of possible ash/flue gas interactions. The results are shown below in Table 3-16, along with a comparison of the Method 29 gas-phase metal results from Sites 1 and 2.



**Table 3-16**  
**Method 29 Metals Results for the FGD Inlet Location**

<b>Parameter</b>	<b>Site 1 Gas Phase Concentration (ppb)</b>	<b>Site 2 Gas Phase Concentration (ppb)</b>	<b>Site 3 Gas Phase Concentration (ppb)</b>	<b>Site 3 Solid Phase Concentration (ppb)*</b>
Aluminum	20.24	10.22	78.29	7568
Antimony	0.17	0.07	0.14	0.24
Arsenic	ND	0.01	0.76	11.65
Barium	0.09	0.08	0.13	11.61
Beryllium	0.27	0.06	0.01	2.64
Cadmium	0.05	0.02	0.01	0.06
Calcium	40.98	15.70	18.91	989
Chromium	0.19	0.12	0.30	9.89
Cobalt	ND	0.02	0.05	1.26
Copper	0.48	0.56	0.12	5.06
Iron	9.08	8.62	18.78	3736
Lead	0.11	0.05	0.05	0.88
Magnesium	3.02	3.05	3.64	318
Manganese	0.49	2.24	1.70	6.36
Molybdenum	0.01	0.02	0.08	3.56
Nickel	0.41	0.17	0.85	8.94
Potassium	89.30	3.17	9.50	592
Selenium	26.79	2.94	45.30	7.75
Silver	0.01	0.01	0.03	0.02
Sodium	191.31	120.24	90.66	290
Strontium	0.09	0.04	0.20	24.76
Thallium	4.52	0.40	7.95	0.04
Titanium	0.64	0.16	1.84	269
Vanadium	0.06	0.00	0.10	12.80
Zinc	2.09	2.30	1.12	8.57

\*Solid phase results are expressed as an equivalent parts per billion in the flue gas on a molar basis.

The most notable result in Table 3-16 is that the measured gas-phase selenium concentration at Site 3 was considerably higher than that measured at Site 1, which was fired with a Texas lignite. Selenium was identified as being a potential contributor to catalyst deactivation at Site 1.

Catalyst regeneration tests were conducted on the Site 3 catalysts to determine if selenium may have contributed to deactivation. These results are discussed in Section 4.

### ***Halogens in the Flue Gas***

In July 2000, gas characterization data were also collected at the FGD inlet location for Cl<sub>2</sub>, HCl, and HF using the EPA Method 26A. These data are summarized in Table 3-17, and show an average of less than 1 ppm of chlorine in the flue gas, 79 ppm of HCl, and 11 ppm of HF. The coal samples from Site 3 were not analyzed for chlorine or fluorine content as part of this project. However, the EPA ICR data for Site 3 showed the coal to average about 0.15 wt % chlorine. The measured Cl<sub>2</sub> and HCl concentrations in the Site 3 flue gas are consistent with a coal with approximately a 0.15 wt % chlorine content.

**Table 3-17**  
**Method 26A Sampling Results for the FGD Inlet Location**

Sample ID	ppm HCl	ppm Cl <sub>2</sub>	ppm HF
M-26A-1	67.8	0.75	10.94
M-26A-2	81.2	0.24	10.99
M-26A-3	88.4	1.07	9.98
Average	79.1	0.69	10.6

### ***Flue Gas SO<sub>3</sub> Concentration***

Flue gas SO<sub>3</sub> gas characterization data were collected using the controlled condensation system sampling method during both the July 2000 and January 2001 gas characterization efforts. The results of the July 2000 measurements are shown in Table 3-18 below.

**Table 3-18**  
**Controlled Condensation System Sampling Results for the FGD Inlet and Outlet Locations, July 2000**

Run	SO <sub>3</sub> Concentration (ppmv)
Inlet-1	2.7
Inlet-2	3.0
Outlet-1	0.61
Outlet-2	0.53
Outlet-Extended Residence Time-1	0.85
Outlet-Extended Residence Time-2	0.62

There are several things to note about the results in Table 3-18. First, the FGD inlet SO<sub>3</sub> concentrations are lower than would typically be expected for a medium sulfur bituminous coal. For bituminous coals, we would typically expect somewhere between 0.5% and 1.5% of the coal sulfur to be converted from SO<sub>2</sub> to SO<sub>3</sub>. Therefore we might have expected SO<sub>3</sub> concentrations in the range of approximately 7 to 20 ppm, although some SO<sub>3</sub> removal across the air heater and ESP would be expected. The measured values are much lower at 2.7 to 3.0 ppm. An initial explanation for the lower values measured was proposed after these July results became available. Site 3 injects ammonia into the flue gas downstream of the air heater and upstream of

the ESP, as a fly ash conditioning agent. The injected ammonia reacts with flue gas  $\text{SO}_3$  to form ammonium bisulfate salts that are collected in the ESP. These salts are sticky, and improve ash cohesiveness and lower ash re-entrainment losses from the ESP. Thus, it was anticipated that the lower-than-expected  $\text{SO}_3$  concentrations at the FGD inlet (ESP outlet) sampling location were because of  $\text{SO}_3$  removal in the ESP as an ammonia salt. However, measurements conducted in January did not confirm this supposition (see below).

The last four results shown in the table represent samples collected at the FGD outlet location in July. Of the four, the first two represent samples collected by the standard controlled condensation method, using a 10-ft (3.0 m) sampling probe, and the last two represent samples collected with additional residence time added between the sampling probe and the thimble filter used to remove fly ash from the sample gas. The additional residence time was added because at the FGD outlet location, all of the  $\text{SO}_3$  in the sample gas is actually present in the form of a condensed sulfuric acid mist. The sample probe and thimble holder are heated to 550°F (288°C) to vaporize this mist before the sample gas passes through the thimble filter. The additional residence time was added during the last two runs to help ensure that the acid mist was completely vaporized, as any mist remaining when the sample gas passes through the thimble might be removed on the thimble surface. The two runs with additional residence times averaged slightly higher  $\text{SO}_3$  concentrations than the two with the normal sampling apparatus (0.7 ppm vs. 0.6 ppm). With only two runs in each configuration, though, it is not clear whether this represents run to run variations or indicates improved  $\text{SO}_3$  recovery with the extended residence time. The two runs with the standard method indicate 80% removal of sulfuric acid mist across the FGD absorber, while the two runs with the extended residence time indicate 74% removal.

In January 2000, flue gas sulfuric acid concentrations were measured again using the CCS method at the two locations mentioned above, and at the air heater inlet and outlet locations. The air heater inlet and outlet locations were sampled simultaneously on one day, and the FGD inlet and outlet locations were sampled simultaneously another day. As were the Ontario Hydro method measurements, the CCS measurements at the air heater inlet and outlet were made with the plant ammonia conditioning system turned off, while the FGD inlet and outlet measurements were made with the ammonia conditioning system in normal operation.

The results of the January CCS measurements are summarized in Table 3-19. The data show the air heater inlet  $\text{SO}_3$  concentrations averaged about 12 to 13 ppm (dry basis). Based on the average  $\text{SO}_2$  concentrations measured along with these samples, the  $\text{SO}_3$  values represent slightly less than 0.7% conversion of  $\text{SO}_2$  to  $\text{SO}_3$  in the boiler and back pass, which is at the low end of conversion percentages for bituminous, pulverized coal fired boilers. The data also show a significant drop in flue gas  $\text{SO}_3$  concentration across the air heater, from 12-13 ppm down to 2-4 ppm (dry basis).

There are two potential reasons for such a drop. One is acid condensation on cool air heater basket surfaces on the “cold” side of the air heater wheel. The estimated acid dew point of the air heater inlet flue gas was calculated to be 275°F (135°C). If the air heater basket surface temperatures on the cold side of the wheel were below 275°F (135°C), sulfuric acid would tend to condense on the basket surfaces. The sulfuric acid concentration measurements were made near the center of the wheel, halfway between the cold and hot sides of the wheel. However, it is possible that basket surfaces were still cool enough at that point to condense sulfuric acid. The other potential reason for a drop in sulfuric acid concentration across the air heater is adsorption

**Table 3-19**  
**Results of CCS Measurements Made at Site 3 During January 2001**

<b>Location/Method Modification</b>	<b>Measured SO<sub>3</sub> Concentration (ppmv)</b>	<b>Average SO<sub>2</sub> Concentration (ppmv, dry)</b>	<b>Average Moisture Content (volume %)</b>
Air Heater Inlet – no modifications	14.4		
	7.8		
	14.0		
	14.5		
	12.4		
	<b>12.6</b>	<b>1890</b>	<b>7.4</b>
Air Heater Inlet – series cyclones	14.7		
	12.3		
	11.9		
	8.8		
	10.8		
	<b>11.7</b>	<b>1790</b>	<b>7.0</b>
Air Heater Outlet – no modifications	5.9		
	3.5		
	3.6		
	3.2		
	3.8		
	<b>4.0</b>	<b>1660</b>	<b>6.2</b>
Air Heater Outlet – series cyclones	2.3		
	2.1		
	1.9		
	1.7		
	2.1		
	<b>2.0</b>	<b>1640</b>	<b>6.8</b>
FGD Inlet – no modifications	4.5		
	5.4		
	5.9		
	6.5		
	5.7		

of sulfuric acid onto fly ash particle surfaces as the gas temperature drops across the air heater. The adsorptive capacity of the fly ash for sulfuric acid is temperature dependent, and the temperature drop should lead to additional adsorption.

**Table 3-19**  
**Results of CCS Measurements Made at Site 3 During January 2001 (continued)**

<b>Location/Method Modification</b>	<b>Measured SO<sub>3</sub> Concentration (ppmv)</b>	<b>Average SO<sub>2</sub> Concentration (ppmv, dry)</b>	<b>Average Moisture Content (volume %)</b>
Average	5.6	1740	6.3
FGD Outlet – 10-ft probe	3.6		
	4.0		
	4.0		
	4.4		
	4.0		
<b>Average</b>	<b>4.0</b>	<b>100</b>	<b>13.1</b>
FGD Outlet – 5 ft probe	3.4		
	3.6		
	3.7		
	4.3		
	3.9		
<b>Average</b>	<b>3.8</b>	<b>99</b>	<b>12.6</b>

At the air heater inlet and outlet locations, two different sampling train configurations were used. One was the standard train, where a quartz-lined probe was inserted perpendicular to the gas stream to collect a representative gas sample. The other used a series of cyclones in-duct on the probe end to separate approximately 95% of the fly ash from the sample gas (the probe by itself removes about 90%), to reduce the amount of ash collected on the thimble in the CCS train. This should presumably reduce the amount of sulfuric acid adsorption on the ash layer and improve the recovery of sulfuric acid from the sample gas. The series cyclones were expected to reduce any tendencies for a low measurement bias in the presence of a full fly ash loading in the sample gas (i.e., sampling upstream of the ESP). However, in both cases, the series cyclone train showed lower concentrations than the standard train, which is opposite the expected effect.

For the air heater inlet location, the small difference between the two trains may just be due to incidental air leakage. The SO<sub>3</sub>, SO<sub>2</sub> and moisture concentrations for the series cyclone train are all 5 to 7% lower than the values from the standard train. This does not appear to be the case for the air heater outlet location, though. It may just be that at the air heater outlet the series cyclone trains happened to be inserted into a port where sulfuric acid concentrations in the flue gas were lower than at the port where the standard configuration was used.

The FGD inlet values (ESP outlet) measured are higher than those measured at the air heater outlet (ESP inlet) even with the standard probe. This is not expected. If anything, some sulfuric acid should be removed by adsorption on ash within the ESP. However, several factors may explain this apparent discrepancy. First, the air heater outlet and FGD inlet were sampled on different days. The average SO<sub>2</sub> concentration measured at the FGD inlet was higher than that measured at the air heater inlet, suggesting higher coal sulfur levels for the former measurement.

Coal samples from the two days confirm this effect; the coal sulfur content on the day of the FGD inlet sampling was 2.84 wt %, while that for the day of the air heater outlet sampling was only 2.21 wt %. Also, it is known that air heater outlet SO<sub>3</sub> concentrations are typically stratified due to the temperature variation of the air heater baskets across the flue gas duct, as mentioned above. It is possible that the ports selected for air heater outlet sampling saw a lower than average flue gas SO<sub>3</sub> concentration, such that after the flue gas was mixed going through the ESP and ID fan, a higher value, reflecting the actual average, would be measured at the FGD inlet.

The FGD inlet SO<sub>3</sub> values measured in January were also lower than those that had been measured in July. Again, this may be a coal sulfur effect; the average coal sulfur content in July was 2.6 wt %, while the coal sample from the day of the FGD inlet CCS runs showed 2.84 wt %.

Note that the air heater inlet concentrations were measured on a day when the plant's ammonia conditioning system was taken out of service, while the FGD inlet values were made with the ammonia system in service. It was expected that the ammonia injection would lead to greatly reduced sulfuric acid concentrations downstream of the ESP, as the objective of ammonia injection is to precipitate ammonium sulfate or bisulfate salts to condition the fly ash for improved ESP performance. The expected decrease in SO<sub>3</sub> concentration across the ESP was not seen in these data, although the coal sulfur variation and potential sample gas stratification at the air heater inlet, as described above, confounded this observation.

At the FGD outlet, two different probe lengths were used for the measurements; both a 5-ft (1.5-m) and a 10-ft (3.0-m) probe length were used. At the FGD outlet location, all of the sulfuric acid in the sample gas is present as a condensed, sub-micron acid mist. To be measured by the CCS method, this mist must be evaporated before the sample gas gets to the heated thimble in the CCS train, as ash reactions with condensed droplets can cause a low bias in the measurement. The two probe lengths were used to provide evidence of whether a 5-ft (1.5-m) probe length is adequate to evaporate all of the acid mist; previous testing and droplet evaporation calculations showed that a 10-ft (3.0-m) length would be more than adequate. The results in Table 3-19 suggest that for this FGD system, the 5-ft (1.5-m) probe length was adequate. The small difference in measured values for the two probe lengths is not considered to be significant.

A comparison of the FGD inlet and outlet sulfuric acid concentrations, which were measured simultaneously, does not show the expected magnitude for the drop in concentration across the FGD absorber. The measurements in July showed lower concentrations at both locations (2.7 to 3.0 ppm at the inlet and 0.5 to 0.8 ppm at the outlet) and an average of approximately 74% to 80% sulfuric acid removal. The data in Table 3-19 indicate only about 30% removal of sulfuric acid across the FGD system. The higher FGD inlet SO<sub>3</sub> concentration in January may be a result of the higher than normal coal sulfur level that day, as mentioned above. However, there is no obvious explanation for the lower SO<sub>3</sub> removal in January. The average SO<sub>2</sub> concentration data for the FGD inlet and outlet locations show 94% SO<sub>2</sub> removal across that absorber, which is near the design level of 95% removal, so it appears to have been operating normally with respect to its effectiveness as a gas contactor.

### ***Coal and Fly Ash Analyses***

Coal and fly ash samples were collected during the flue gas characterization testing. Results from mercury analyses samples are listed in Table 3-20. These show fairly wide variations in mercury

**Table 3-20**  
**Results of Mercury Analysis of Site 3 Coal and Fly Ash Samples**

Sample Date	Mercury Concentration (ppm)		
	Coal	Mill Rejects	ESP ash
6/28/00	0.215	-	0.309
7/11/00	0.439	-	0.738 <sup>1</sup>
7/11/00	-	-	0.470 <sup>2</sup>
10/03/00	0.553	-	-
1/23/01	0.513	0.963	-
1/24/01	0.382	0.479	0.335
1/25/01	0.458	3.05	-
1/26/01	0.405	-	0.272 <sup>3</sup>

<sup>1</sup>Hopper 12.

<sup>2</sup>Hopper 13.

<sup>3</sup>Sample collected while the ammonia injection system was not operating.

concentrations for both sample types. Fly ash samples obtained at the same time from different hoppers showed appreciable differences. Part of the difference may be related to sample homogeneity and difficulties associated with obtaining representative fly ash samples from the individual hoppers. Regardless, results indicate an appreciable adsorption of mercury on the fly ash. It is not currently known what factors determine the ability of fly ash to remove mercury from flue gas, although factors that appear important include flue gas temperature and composition, fly ash exposure time to flue gas, and fly ash LOI (carbon content).

The coal samples showed relatively high mercury concentrations of 0.2 ppm or greater. Most showed concentrations in the range of 0.38 to 0.55 ppm. These coal mercury concentrations would lead to an expectation of flue gas total mercury concentrations in the range of approximately 30 to 50  $\mu\text{g}/\text{Nm}^3$ . This is consistent with the January Ontario Hydro total mercury concentration data from the air heater inlet location.

A second observation is that the ESP ash sample mercury concentrations are nearly as high as those in the original coal samples. Since the ash represents about 12 to 16% of the as-received coal, mercury adsorbed on these ash samples most likely represents 10 to 15% of the mercury in the coal. There was some speculation that ammonia injection might enhance mercury adsorption on the fly ash collected in the ESP. The mercury content of the fly ash samples from 1/24 (ammonia on) and 1/26 (ammonia off) show about a 20% reduction in ash mercury content when the ammonia injection system was shutdown. After taking the mercury and ash contents of these two coal samples into account, the amount of mercury collected with the fly ash could have been reduced by almost 40%. This is a potentially significant effect.

A third observation is that the coal pulverizer rejects (presumably pyrites) are higher in mercury concentration than the overall coal samples; in one case, significantly higher. This suggests an enrichment of mercury with pyrites in the coal. However, the quantity of mill rejects is estimated to be relatively minor (less than 1% of the coal throughput) so this apparent enrichment should not greatly impact a mercury balance around the power plant.

Fly ash LOI concentrations were measured in an attempt to explain the relatively high mercury levels in the ash. These results are summarized in Table 3-21. The LOI values are relatively high (approximately 5 to 8%) and may account for the significant mercury adsorption that appears to occur.

**Table 3-21**  
**Results of LOI Analyses on Fly Ash Samples from June through November 2000**

Sample Type	Sample Date	Loss on Ignition (wt %)*
Fly Ash	6/28/00	7.2
Fly Ash	7/11/00	8.3
Fly Ash (2A9-16)	9/26/00	4.6
Fly Ash (2B9-16)	9/26/00	4.6
Fly Ash (2A9-16)	10/03/00	6.2
Fly Ash (2B9-16)	10/03/00	5.6
Fly Ash	11/14/00	6.9

\* Average of two analyses.

The results of ultimate and proximate analyses of coal samples from June, July, and January 2001 are summarized in Table 3-22. The results show the June and July coal samples to be consistent in sulfur content, at about 2.6 wt % in the coal, producing about 4.2 to 4.3 lb/MM Btu of SO<sub>2</sub>. The January results show a much wider range of coal quality. The sample from January 24 has the highest ash and sulfur content, and the lowest heat content of the five samples for which results are available. The sample from the next day, January 25, has 25% less sulfur and 20% less ash than the January 24 sample. The January 26 sample has an even lower sulfur content, almost 33% less than the sulfur content for January 24. This illustrates the relatively wide range of coal quality that was encountered that week in January, a situation that was reported to us by plant personnel at the time and that is supported by the plant coal logs for this time period.

**Table 3-22**  
**Results of Ultimate Analyses of Coal Samples from Site 3 (all values as received basis)**

Sample Date	Ultimate Analysis (wt. % as received)							Heat Content (Btu/lb)*
	Moisture	Carbon	Hydrogen	Nitrogen	Sulfur	Ash	Oxygen	
6/28/00	5.04	69.66	3.99	1.22	2.62	13.02	4.55	12,220
7/11/00	4.68	71.23	4.41	1.29	2.62	10.73	5.04	12,510
1/23/01	6.66	66.46	4.02	1.21	2.84	14.74	4.07	12,093
1/24/01	5.80	68.08	3.85	1.21	2.92	16.02	2.12	11,949
1/25/01	7.88	68.26	4.17	1.24	2.21	12.80	3.44	12,079
1/26/01	7.46	68.26	4.09	1.21	1.97	13.11	3.90	11,910

\*12,000 Btu/lb is equivalent to 25.3 k-joules/g.

\*\*To be determined later, sample was not received from the plant and a new sample has been requested.



The coal and ash analysis results were used in a combustion calculation to estimate coal, flue gas and fly ash rates, then compared with the previous fly ash and coal mercury concentration data collected at Site 3 to calculate mercury mass balance closures. The mass balance closures are shown in Table 3-23. Note that the June and July coal and ash samples were collected during short-term catalyst tests; due to a miscommunication with the plant, coal and ash samples were not acquired for the flue gas characterization period in July. The mass balance closures shown for June and July in Table 3-23 are based on flue gas total mercury content measured by the EPRI field analyzer rather than by the Ontario Hydro Method or Method 29. For the coal and ash samples collected on January 24, there are corresponding Ontario Hydro method flue gas

**Table 3-23**  
**Summary of Mercury Balance Calculations for Site 3, June 2000 through January 2001**

	6/28/00	7/11/00	1/24/01	1/26/01
Coal Hg Content, ppm dry basis	0.22	0.44	0.38	0.41
Coal Fired, tons/hr (1000 kg/hr)	340 (309)	332 (302)	377 (343)	325 (296)
Hg in Coal Fired, lb/hr (g/hr)	0.14 (63)	0.28 (126)	0.29 (130)	0.26 (119)
Fly Ash Hg Content, ppm	0.31	0.60	0.34	- *
Fly Ash Production Rate, lb/hr (kg/hr)	71,000 (32,000)	57,000 (26,000)	97,000 (44,000)	- *
Hg in Fly Ash, lb/hr (g/hr)	0.02 (10)	0.03 (16)	0.03 (16)	- *
Hg in Bottom Ash, lb/hr, assumed (g/hr)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Hg in Coal Mill Rejects, lb/hr (g/hr)	-	-	<0.01 (<1)	<0.01 (<1)
Hg in FGD Inlet Gas, $\mu\text{g}/\text{Nm}^3$	15.7	22.7	8.0	37.7*
Flue Gas Rate, $10^6$ dscfm ( $\text{Nm}^3/\text{s}$ )	1.90 (898)	1.91 (903)	1.82 (860)	1.58 (747)*
Hg in FGD Inlet Flue Gas, lb/hr (g/hr)	0.11 (48)	0.15 (70)	0.06 (25)	0.21 (96)*
Hg in Flue Gas + Ash, lb/hr (g/hr)	0.13 (58)	0.19 (85)	0.09 (42)	0.21 (96)*
Hg Balance Closure, %	92	68	32	80*

\*Material balance calculated for air heater inlet location. Mercury in ash contribution not included.

mercury concentrations at the ESP outlet/FGD inlet location. These values were, in turn, used for the mercury balance calculations for that date.

The mercury material balance closures in Table 3-23 show relatively good closure (92%) for the samples from June 28, but poorer closure (68%) for the samples from July 11. With the wide range of observed flue gas, coal, and ash mercury contents at Site 3, and the observation that flue gas total mercury concentrations can vary markedly throughout the day, it would be expected that tight material balance closures would be difficult to achieve at this site. That is, it would be difficult to collect coal and ash samples that are known to be representative of the flue gas at any one point during the day of collection. Coal and ash samples collected at one time during the day may not correlate well with the flue gas at the time inlet mercury concentrations are measured. That is most likely the reason the mercury mass balance closure for July 11 is not closer to 100%.

The mercury balance data for January 24 show a very poor closure. The amount of mercury accounted for in the coal mill rejects, ESP outlet/FGD inlet flue gas, and in the fly ash collected in the ESP account for only 32% of the mercury in the coal fired in the Site 3 boiler. There are several potential reasons for this poor closure. Perhaps the best potential explanation is that the coal quality was known to be quite variable over this time period, much more so than during the June and July measurement periods. Presumably the coal quality variations also greatly impacted coal mercury content. The poor material balance closure could well be due to coal, ash and Ontario Hydro flue gas samples being collected at different times during the day, and thus not reflecting a common coal mercury content. Furthermore, the coal and ash samples are merely grab samples from a single location for each. With variable coal quality, and given the size of the boiler at Site 3 (>750 MW) it is likely that grab samples are poor representations of the average compositions of these large process streams at any one time.

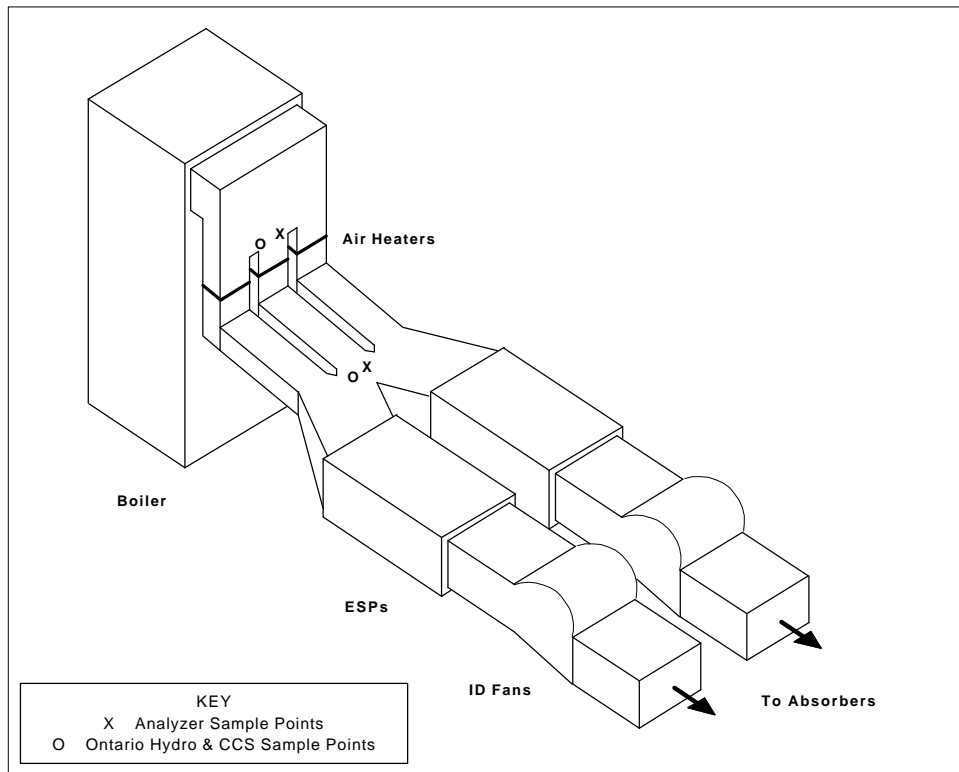
The mercury balance for January 26 was conducted on a different basis than the other balances. For this balance, we have air heater inlet flue gas mercury concentration data, so the balance was calculated for that location rather than for the FGD inlet. For the balance at this location, we assumed there would not be an appreciable amount of mercury in the fly ash at this temperature (650°F). Consequently, the balance compares only the coal mercury content to the air heater inlet flue gas mercury content, avoiding the complication of having to collect representative fly ash samples to account for mercury removal across the air heater and ESP. This mercury balance closes relatively well (within the value of  $\pm 20\%$  that is typically regarded as good closure for trace metal balances around full-scale power plants), even disregarding any mercury that might already be adsorbed by the fly ash at this location. This improved closure when comparing only flue gas measurements and a grab coal sample analysis suggests that the poor closures for the balances on July 11 and January 24 are, in fact, due to difficulties in collecting coal, fly ash, and flue gas samples all representative of the same conditions.

### ***Continuous Monitoring for Flue Gas Mercury Content***

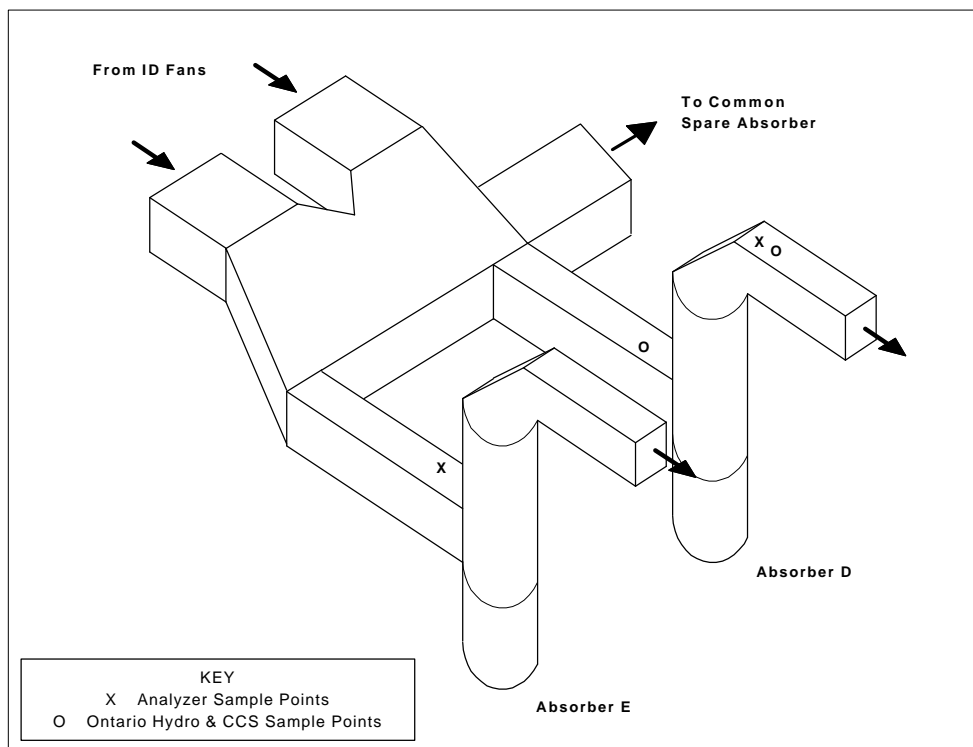
During the test period in late January and early February 2001, two semi-continuous mercury emissions monitors (SCEM units) were used at Site 3 to characterize the flue gas at four different locations: the air heater inlet, the air heater outlet/ESP inlet, the ESP outlet/FGD inlet and the FGD outlet. Measurements were made with the intent of characterizing the effect of temperature, particulate removal, and scrubbing on flue gas mercury concentration and speciation.

Measurements were also conducted by the draft Ontario Hydro method to verify mercury concentrations/speciation throughout the process. Figures 3-5 and 3-6 show the sample locations for both the analyzer and Ontario Hydro methods. In both figures, an 'X' indicates a sample location for the mercury analyzer (SCEM unit), and an 'O' indicates a sample location for the Ontario Hydro method. Figure 3-5 depicts the process upstream of the ID Fans and Figure 3-6 depicts the process downstream of the ID Fans.

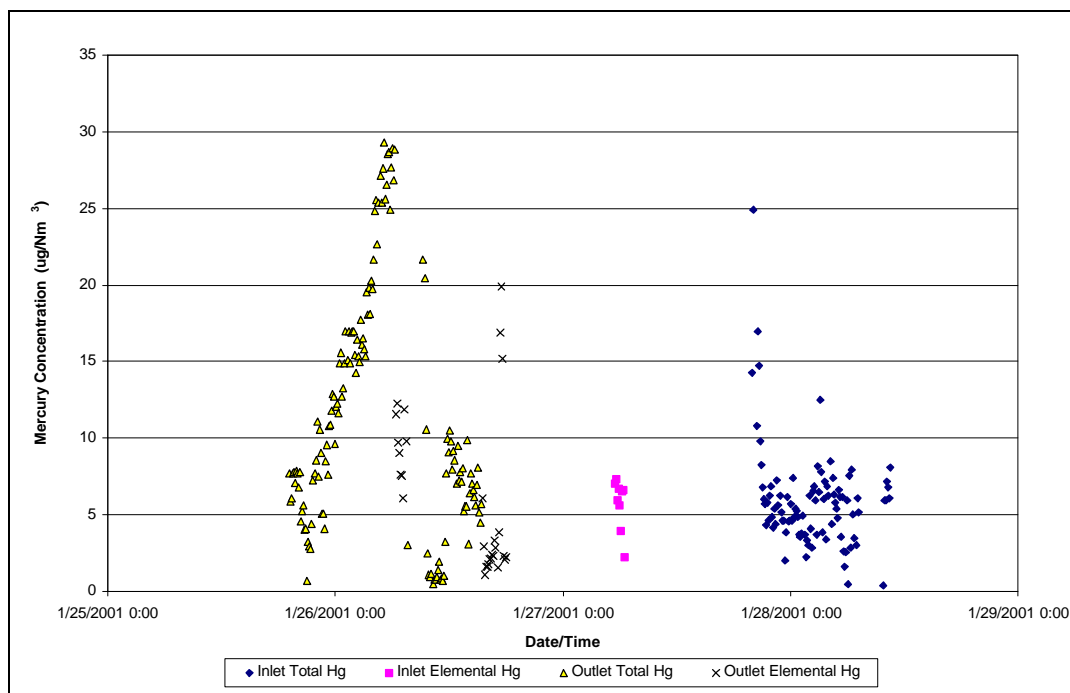
Figure 3-7 shows the mercury concentrations and speciation, as measured by the SCEM, at the air heater inlet and outlet locations. Based on the results of previous research, it was expected that the flue gas mercury concentration would decrease across the air heater. This is due to the mechanism for adsorption of mercury onto fly ash being more favorable at lower temperatures. Hence, decreasing the temperature of the gas from 650°F to 300°F would be expected to result in greater mercury adsorption and lower flue gas mercury concentrations.



**Figure 3-5**  
**Sample Locations Located Upstream of the ID Fans**



**Figure 3-6**  
**Sample Locations Located Downstream of the ID Fans**



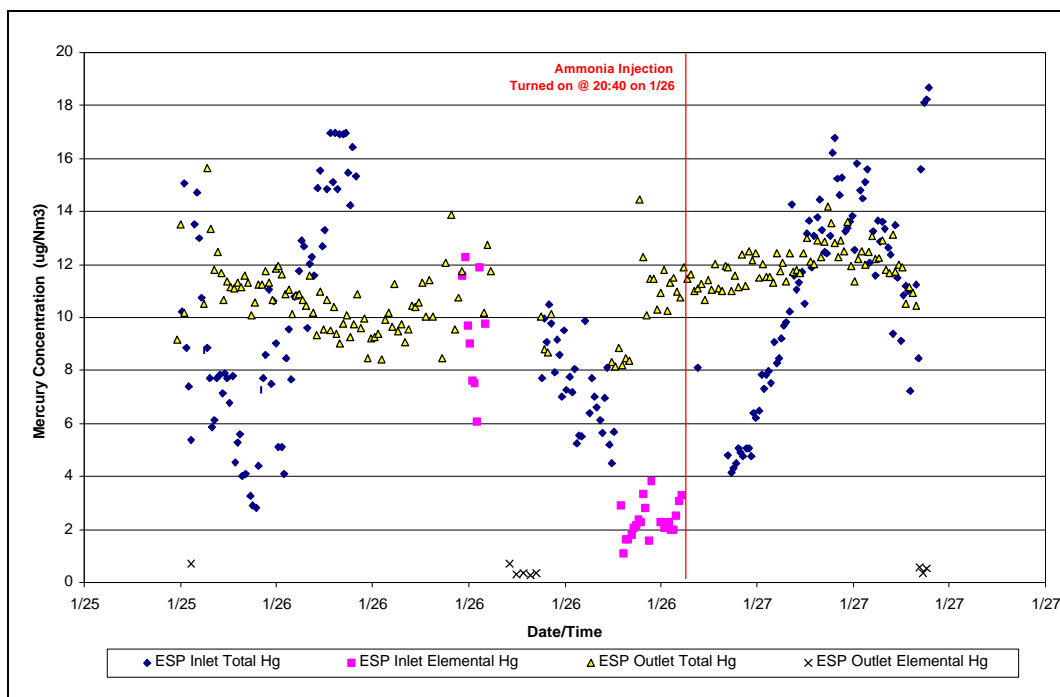
**Figure 3-7**  
**Mercury Concentration/Speciation at Air heater Inlet and Outlet**

Based on Figure 3-7, it is difficult to tell the effect of the temperature decrease on mercury concentration. Changes in the coal fired and possibly combustion variations resulted in large fluctuations in mercury concentrations over this time period. These fluctuations made comparing measurements made at different times difficult. Possible analytical problems further hindered the ability to compare mercury levels at the two locations. Mainly, analytical problems were apparent at the air heater outlet location, where continual shifts in the mercury levels were measured. Due to these variances, drawing a reliable conclusion as to the effect of decreased temperature on mercury levels was not possible based on SCEM results.

Figure 3-8 compares flue gas mercury concentrations and speciation across the ESP. Due to the ESP outlet location having a greater residence time over which mercury can be adsorbed by the fly ash, mercury levels would again be expected to be lower at the outlet location.

In Figure 3-8, the analytical problems at the ESP inlet (air heater outlet) are more apparent. While the mercury concentration at the ESP inlet varies greatly, measurements made simultaneously at the ESP outlet remain steady. Again, the uncertainty in the analytical results at the ESP inlet location makes comparing mercury levels at the two locations difficult.

Figure 3-9 compares mercury measurements made across the FGD system. Due to oxidized mercury being soluble in water, the majority of the oxidized mercury should be removed in the absorber, resulting in predominantly elemental mercury in the outlet gas.



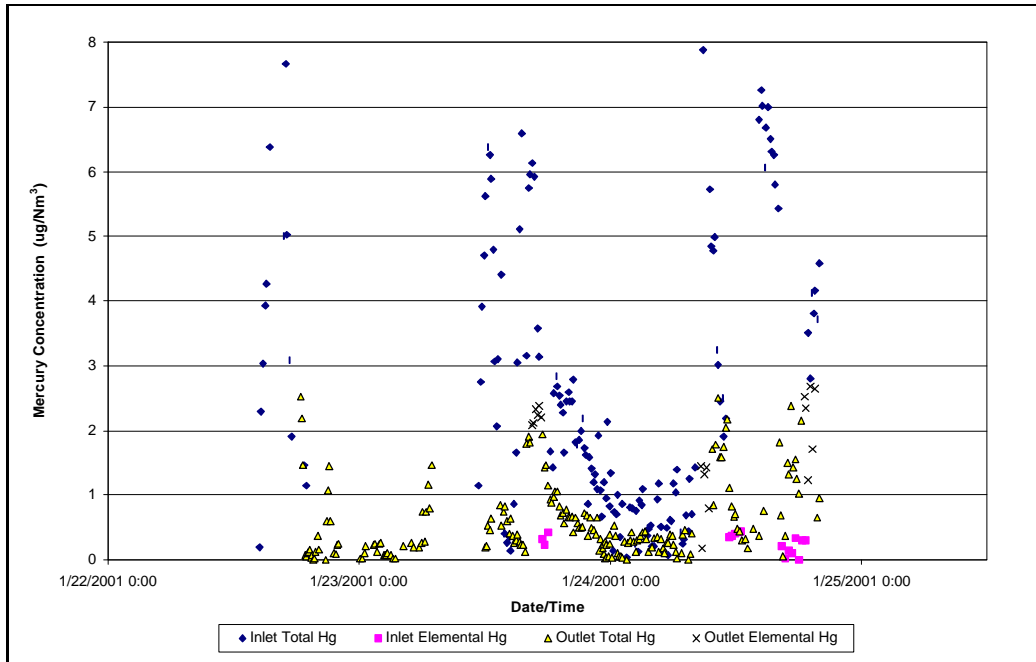
**Figure 3-8**  
**Mercury Concentration/Speciation ESP Inlet and Outlet**

As evident in Figure 3-9, there was a reduction in total mercury concentration across the FGD unit. Furthermore, the absorber outlet gas appears to be comprised of strictly elemental mercury. While there are huge variations in FGD inlet mercury concentrations, with values ranging from below 1  $\mu\text{g}/\text{Nm}^3$  to greater than 7  $\mu\text{g}/\text{Nm}^3$ , the outlet concentrations tended to track with the inlet. Typically, the observed mercury removal across the FGD system in these SCEM results ranged from 50% to greater than 80%.

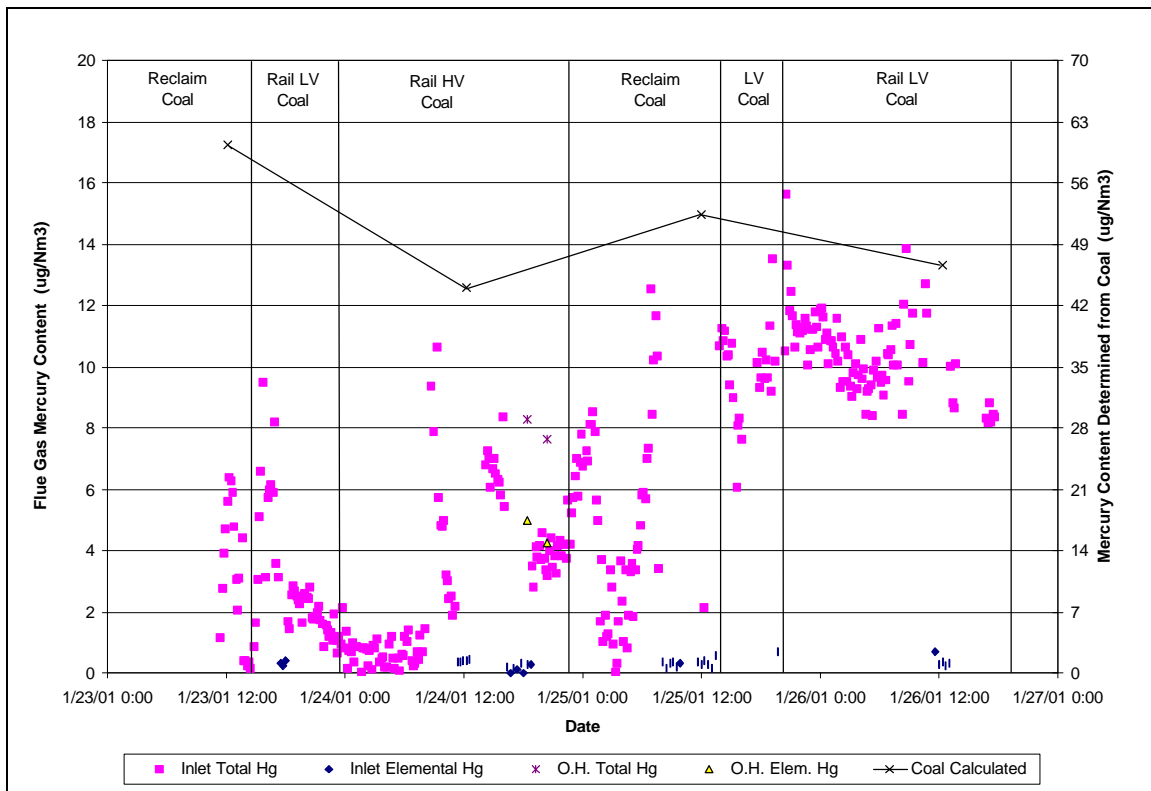
### **Process Correlations**

During the testing in late January and early February, process data were collected to determine whether any process conditions correlated with flue gas mercury levels. The process data collected included: which coal was fired, unit load, total unit coal flow, boiler exit  $\text{O}_2$  and carbon monoxide, FGD inlet  $\text{SO}_2$  and opacity, stack  $\text{NO}_x$  and  $\text{CO}_2$ , economizer outlet temperature, air heater outlet temperature, and absorber inlet temperature. Of the process data collected over this time period, only the coal fired and opacity seemed to show any correlation with flue gas mercury concentrations.

As described earlier in this section, the measured coal sample mercury concentrations varied significantly during the one-week period over which mercury concentrations were measured in the flue gas. The highest coal sulfur content was over 30% greater than the lowest measured for the coal samples from that week. However, the flue gas mercury concentrations measured at the FGD inlet location varied by a much higher percentage, with the highest concentrations being an order of magnitude greater than the lowest. Also, the FGD inlet mercury concentrations, as measured by the mercury SCEM and by the Ontario Hydro method, were much lower than what was predicted based on the coal mercury concentrations. This is illustrated in Figure 3-10, which



**Figure 3-9**  
**Mercury Concentration/Speciation at FGD Inlet and Outlet**



**Figure 3-10**  
**Relationship between Coal Mercury Content and Flue Gas Mercury Concentrations at the FGD Inlet**

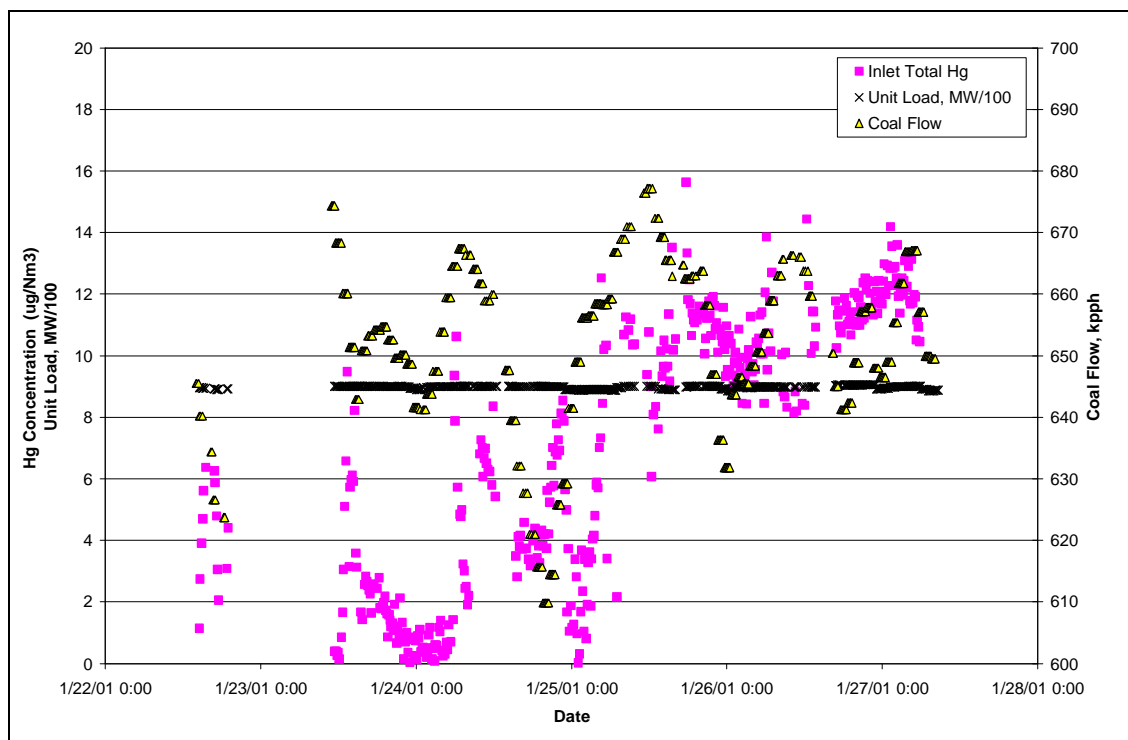
shows predicted concentrations in the range of 40 to 60  $\mu\text{g}/\text{Nm}^3$  while FGD inlet concentrations were measured to range from less than 1 to about 16  $\mu\text{g}/\text{Nm}^3$ .

As described earlier in this section, the lower than predicted total mercury concentrations at the FGD inlet location have been attributed to mercury adsorption on the fly ash. What is evident from the data plotted in Figure 3-10 is that the percent of the mercury adsorbed on the fly ash varied markedly during the week. The apparent mercury removal percentages upstream of the FGD inlet location varied from about 75% on January 26 to greater than 90% during periods from the afternoon of January 23 through late on January 24.

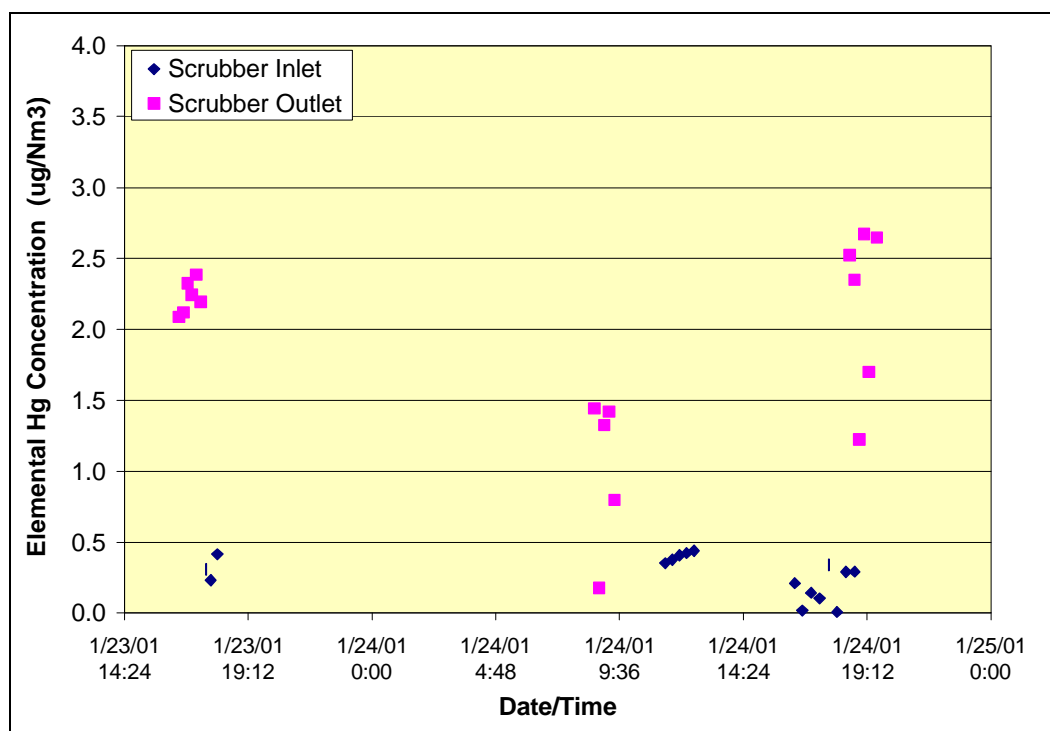
Figure 3-10 also shows the approximate times that various coals were fired in the Site 3 boiler during the week. The coals included both low volatility (LV) and high volatility (HV) types that were either loaded into the Site 3 coal bunkers from trains, or were reclaimed off of the coal pile. Because the changes in coal fired were quite frequent over this period, it is difficult to attribute FGD inlet mercury concentrations to a given fuel. The time period shown for each coal is an estimate of when that coal was fired, taking into account the time each coal began loading into the bunkers and the approximate coal residence time in the bunkers. These estimates are only approximate, though, because effects such as “rat-holing” in the bunkers, differences in coal density and heat content, and variations in bunker inventories when a new coal was loaded would impact when the new coal started firing. Also, coal sloughing off of bunker walls could add a spike of the previous coal after a new coal had started firing.

While it may not be possible to relate FGD inlet mercury concentrations or apparent mercury fly ash removal percentages to particular coals, the data in Figure 3-10 illustrate that the coals fired were being changed at approximately the same frequency that step changes in mercury concentration were being measured. Further indication that variations in coal type resulted in varying flue gas mercury concentrations is evident by the correlation between coal flow and mercury concentrations. Figure 3-11 plots the FGD inlet mercury concentration data along with coal flow and unit load. Whereas the unit load was relatively stable, the coal flow varied significantly over this time, which is an indication of the widely varying coal quality (e.g., variations in the as-fired coal heating value) during this time period. This plot lends greater credibility to speculations that coal quality variations caused the wide variations in measured FGD inlet total mercury concentrations.

Figure 3-12 is a plot of FGD inlet and outlet elemental mercury concentrations during the same time period as in Figure 3-11. The FGD outlet elemental mercury concentrations are considerably higher than at the inlet. The difference between the inlet and outlet elemental mercury concentrations is higher than would be expected based on the Ontario Hydro results. However, the two locations were not monitored for elemental mercury concentration at exactly the same times. Since the total (and presumably elemental) mercury concentrations were observed to vary markedly during this general time period, it is possible that the FGD outlet locations was measured for elemental mercury concentration during periods where the total mercury concentrations were higher than when the inlet elemental mercury was measured. Also, note that even at the FGD outlet location, the elemental mercury concentrations measured were considerably lower than were indicated by the Ontario Hydro method. It is apparent that some unknown effect was confounding either the SCCEM or Ontario Hydro method results, or possibly both.



**Figure 3-11**  
**FGD Inlet Total Mercury by SCEM vs. Coal Flow and Unit Load**



**Figure 3-12**  
**Results of Simultaneous FGD Inlet and Outlet Gas Monitoring for Total Mercury Concentration by Mercury SCEM**



Since the coal fired was observed to have an effect on the flue gas mercury concentration, the remaining process data were only compared to flue gas mercury measurements made during time periods when the same coal type was fired. Based on the data, the only other correlation that could be found was the effect of opacity on flue gas mercury. Figure 3-13 shows the relationship between opacity, as measured at the FGD inlet, and flue gas mercury concentration.



**Figure 3-13**  
**Relationship between Opacity and Flue Gas Mercury Concentrations at the FGD Inlet**

As seen in the Figure 3-13, increased opacity seems to correspond to decreased flue gas mercury concentrations. There are two possible reasons for this phenomena: a change in combustion resulted in a higher LOI content of the fly ash, or a greater amount of fly ash provided more surface area for mercury adsorption to occur. Carbon is more difficult to remove in an ESP than fly ash due to its low resistivity, which can result in carbon being re-entrained into the flue gas after it is collected. The inability of the ESP to effectively remove the carbon content of a fly ash can result in increased opacity. Unburned carbon levels have been experimentally proven to correlate to mercury adsorption, with higher levels resulting in greater adsorption. Hence, higher LOI content typically results in lower flue gas mercury levels. A higher ash content coal could also result in increased opacity, as ESPs typically remove a relatively fixed percentage of the inlet particulate. A greater amount of fly ash in the ESP inlet flue gas would provide more surface area for mercury adsorption to occur, and would tend to lower flue gas mercury content while increasing outlet opacity.

# 4

## LABORATORY TEST RESULTS

Laboratory testing has been conducted throughout Phase II to support the field tests. For Site 3, laboratory tests have been conducted to screen catalysts for effectiveness at simulated Site 3 flue gas conditions and some alternate flue gas conditions, to attempt regeneration of catalysts recovered from the long-term sand bed reactor tests at Site 3, and to determine catalyst deactivation mechanisms. Each of these laboratory test efforts is discussed below.

### Catalyst Screening Tests

Prior to field testing, bench-scale tests are conducted to screen catalyst materials at flue gas conditions similar to each test site. This allows the field effort to focus on only the more active catalysts for a particular flue gas composition. Table 4-1 lists the gas compositions for the Site 3 simulation tests. Actual gas compositions that were subsequently measured at Site 3 are also shown in the table. In most instances the assumed values used for the simulation gas were close to the values that were later measured for the actual flue gas. The exception was for elemental mercury, where the laboratory simulation gas contained more than the Site 3 flue gas to better ensure that catalyst performance could be accurately measured.

**Table 4-1**  
**Simulated Flue Gas Compositions for Bench-Scale Tests**

Flue Gas Parameter	Site 3 Simulation Gas	Measured Site 3 Gas Conditions
O <sub>2</sub> (%)	6	*
SO <sub>2</sub> (ppm)	1600	1530 – 1750
SO <sub>3</sub> (ppm)	0	2.7-5.6
CO <sub>2</sub> (%)	12	*
HCl (ppm)	50	74
NO <sub>x</sub> (ppm)	400	*
H <sub>2</sub> O (%)	7	6.2 – 6.8
Hg <sup>0</sup> (µg/Nm <sup>3</sup> )	40 - 70	<1 – 7

\*Not measured

Several carbon, ash, and metal catalyst materials were tested for oxidation activity in this simulated flue gas at 300°F (149°C). The results of these tests are summarized in Table 4-2. Results are also presented in the table for 275°F (135°C) and 325°F (163°C) gas temperatures. These are previous results from a separate EPRI project.

For some materials there are no results at a 300°F (149°C) gas temperature, which is the temperature at which the Site 3 field tests were conducted. However, it is probably safe to interpolate between the 275°F (135°C) and 325°F (163°C) temperature results for those materials.

**Table 4-2**  
**Laboratory Oxidation Test Results at Three Simulation Gas Temperatures**

Generic ID	Elemental Hg Oxidation (%)		
	275°F (135°C)	300°F (149°C)	325°F (163°C)
<b>Carbon Samples</b>			
Carbon #1	94	98	95
Carbon #2	100	-	100
Carbon #3	95	-	95
Carbon #4	94	81	78
Carbon #5	21	-	16
Carbon #5a	94	-	87
Carbon #6	99	-	95
<b>Fly Ash Samples</b>			
Subbituminous Ash #1	27	5	-
Subbituminous Ash #2	38	-	33
Subbituminous Ash #3	83	-	89
Subbituminous Ash #4	92	78	52
Subbituminous Ash #5	84	84	70
Bituminous Ash #1	-	36	-
Bituminous Ash #2a - Cyclone	67	-	76
Bituminous Ash #3	-	14	-
Bituminous Ash #3	87	86	72
Lignite Ash #1	-	0	-
Lignite Ash #2	22	27	-
Oil-Fired Ash	-	4	-
<b>Metal Catalyst Samples</b>			
Alumina	-	0	-
Fe #1	-	88	-
Fe #2	-	50	-
Fe #3	-	95	-
Fe #5	-	83	-
Ni #1	-	0	-
Pd #1	-	92	-
Pd #2	-	95	-
Pd #3	-	96	-
SCR Catalyst	-	57	-
Zn #1	-	0	-

With many of the carbons and ashes, a general trend of decreasing oxidation with increasing temperature was observed. The oxidation percentage for these samples at 300°F (149°C) often fell between those at the two other temperatures and was typically greater than the oxidation results obtained at 325°F (135°C). For screening purposes, this trend supports the assumption that the oxidation level at 300°F (149°C) for samples with no data at that temperature can be interpolated from data obtained at the higher and lower temperatures.

The results in Table 4-2 identified a number of materials that would be expected to result in approximately 80% oxidation of elemental mercury or greater in the field. Most of these materials were evaluated in short-term catalyst screening tests in the field at Site 3. Two of the active materials, Pd #2 and Pd #3, showed high elemental mercury oxidation percentages in the laboratory, but since these materials are similar in composition, performance, and presumably cost to the commercial Pd #1 catalyst, they were not further tested in the field.

Table 4-3 compares the laboratory results from Table 4-1 with the results of the short-term catalyst screening tests, as reported in Section 3. The carbons were generally less active in the field than in the simulation gas environment, particularly Carbon #4. Similarly, the fly ashes were all less active in the field than in the laboratory tests. Metal catalyst performance, though, was essentially the same in the field as in the laboratory for the Fe #1 and Pd #1 materials, with the field result for the SCR catalyst actually showing better performance than in the simulation gas.

## **Catalyst Regeneration Tests**

Bench-scale tests were also carried out to investigate the possibility of regenerating catalysts. Previous results<sup>1,2,3</sup> were promising, showing that catalysts deactivated during long-term tests at Site 1 and Site 2 were effectively regenerated after being purged in N<sub>2</sub> or CO<sub>2</sub> at elevated temperatures.

Some catalyst regeneration tests were conducted on materials recovered from long-term testing at Site 3. The testing involved measuring the oxidation performance of recovered samples, then regenerating those samples in heated nitrogen. Regenerated samples were then tested for mercury adsorption and oxidation in simulated flue gas. The results of these tests are discussed below.

### **Laboratory Testing of Site 3 Long-term Catalysts**

Catalyst materials from the long-term test at Site 3 were recovered from the field and tested in the laboratory to verify oxidation and adsorption capacities. In these tests, a portion of the recovered sample was placed in a fixed-bed configuration and reacted with simulated flue gas at 300°F (149°C). Table 4-4 displays the results of the laboratory tests on recovered catalysts compared to the November field test results. The latter represent the last oxidation performance data that were measured for the long-term test materials.

All of the recovered catalysts showed measurable adsorption capacity in the laboratory, while they had appeared to be at or near mercury adsorption equilibrium in the field. This indicates that some regeneration occurred after removing the catalysts from the Site 3 flue gas and exposing them to simulated flue gas. For the Subbituminous Ash #5, the adsorption capacity was so great

**Table 4-3**  
**Comparison of Laboratory Oxidation Test Results at 300°F (149°C) with Site 3 Short-term Screening Test Results**

Generic ID	Elemental Hg Oxidation (%)	
	Lab Result	Field Result
<b>Carbon Samples</b>		
Carbon #1	98	73
Carbon #2	100*	**
Carbon #3	95*	93
Carbon #4	81	7
Carbon #6	97*	62
<b>Fly Ash Samples</b>		
Subbituminous Ash #4	78	37
Subbituminous Ash #5	84	44
Bituminous Ash #3	86	-11
<b>Metal Catalyst Samples</b>		
Fe #1	88	90
Fe #5	83	**
Pd #1	92	92
SCR Catalyst	57	87

\*Interpolated from 275°F (135°C) and 325°F (163°C) results.

\*\*Not measured because upstream bed in test apparatus maintained high activity for mercury oxidation over the duration of the short-term test.

**Table 4-4**  
**Comparison of Laboratory Test Results for Recovered Catalysts to Site 3 Long Term Results**

Catalyst	Laboratory Results for Recovered Catalysts			November Field Results, Elemental Hg Oxidation (%)
	Oxidized Hg Adsorption Capacity (mg/g sorbent)	Elemental Hg Adsorption Capacity (mg/g sorbent)	Elemental Hg Oxidation (%)	
Fe #1	>220	9	18	45
Carbon #6	490	100	91	85
Pd #1	54	3	72 <sup>1,2</sup>	87 <sup>3</sup>
Subbituminous Ash #5	150	>170	-	-
Sand Bed Blank	<1	<1	1	36

<sup>1</sup> Loss of flow across the catalyst bed in field apparatus may have adversely affected performance.

<sup>2</sup> Both catalyst beds combined prior to analysis.

<sup>3</sup> First of two catalyst beds in series.

that after 24 hours of exposure to simulation gas, it was not possible to measure an oxidation percentage, as too high a percentage of the total mercury was still being adsorbed. This is similar to results observed with the original sample prior to the long-term test.

Due to the extended time period between the most recent field results (November 2000) and when the catalysts were actually removed from the process (January 2001), comparing the field oxidation results to the laboratory results may not be meaningful. The laboratory results show that two of the three catalysts for which oxidation performance was measured were still capable of oxidizing greater than 70% of the inlet elemental mercury, with the Carbon #6 oxidizing 91% and the Pd #1 oxidizing 72%. The Fe #1 material reflected a continued loss of activity with time at Site 3, as had been seen in the October and November results. However, the laboratory performance of these materials is not necessarily an indicator of their end-of-test performance, as catalysts recovered from the previous two sites generally performed better in the laboratory simulation gas than they had when recovered from the field apparatus. It is speculated that trace species may desorb from the recovered catalysts into the simulation gas, which does not contain such species, partially restoring catalyst activity.

Also, for the Pd #1, it must be noted that a plug in the field apparatus resulted in the loss of flue gas flow across the two sand beds in series. It is likely that in this zero-flow situation, but in the presence of an oxidation catalyst and an ample supply of oxidizing species in the trapped flue gas (e.g., oxygen), the Pd #1 activity was adversely affected by species such as sulfuric acid forming and condensing onto the catalyst surface.

The mercury oxidation data for the sand bed recovered from the Site 3 long-term test are somewhat puzzling. In the field, the oxidation measured across this sand bed “blank” continued to increase with time, with the November percentage measuring at 36% and higher percentages being measured later in the test. However, in the lab, the measured oxidation of elemental mercury across the sand was insignificant, at 1%.

There are at least two possible explanations for this performance. One is that some trace species in the actual flue gas (e.g., selenium) was interacting with the sand to produce a catalytic effect. The laboratory simulation gas was relatively pure and did not contain such trace species. The other, more likely explanation is a fly ash effect. The FGD inlet flue gas at Site 3 contained considerably more fly ash than did the flue gases at Sites 1 and 2. The fly ash at Site 3 was measured to have a relatively high LOI content (typically greater than 5%) and was observed to be reactive for adsorbing and oxidizing mercury. Although the long-term test apparatus had a filter upstream of the catalyst beds to remove fly ash, the filter paper used had a 0.45-micron pore size. It is possible that sub-micron fly ash particles, rich in carbon, penetrated the filter with time. Such particles would collect on the walls of the quartz tubing between the filter and the upstream sand beds, and would collect on the quartz wool plug at the inlet to each bed. It is speculated that the observed high mercury oxidation percentages seen across the sand bed as the long-term test progressed was due to fly ash particle buildup with time, and that the oxidation was actually occurring upstream of the sand bed itself. The low elemental mercury concentrations measured in the flue gas at the sand bed inlet (filter outlet) would tend to exacerbate such an effect.

## ***Catalyst Regeneration***

Bench-scale tests were carried out to investigate the possibility of regenerating catalysts recovered from the long-term test at Site 3. Previous results<sup>1,2,3</sup> were promising, showing that catalysts deactivated during long-term tests at Site 1 and Site 2 were effectively regenerated after being purged in N<sub>2</sub> or CO<sub>2</sub> at elevated temperatures.

Catalyst regeneration testing was conducted on materials recovered from long-term testing at Site 3, as well. Based on the post-field-testing laboratory results, as reported in Table 4-4, the Pd #1 and Fe #1 catalysts were selected for regeneration. The Carbon #6 remained highly active and did not appear to warrant regeneration. Subbituminous Ash #5 also appeared to be very active. Since the sample continued to adsorb mercury during the tests summarized in Table 4-4, its elemental mercury oxidation activity could not be measured.

The Pd #1 and Fe #1 catalyst materials were regenerated by heating samples to 700°F and purging them with nitrogen for two hours. The regenerated catalysts were then tested in the laboratory for elemental mercury adsorption and oxidation. Results for the regenerated materials are summarized in Table 4-5. The results in Table 4-5 show that the Pd #1 material was effectively regenerated under these conditions, but the Fe #1 was not. The regenerated samples did not show significant adsorption capacity for elemental mercury.

**Table 4-5**  
**Catalyst Activity Results for Regenerated Catalyst Samples from Site 3**

<b>Catalyst Material</b>	<b>Elemental Hg Adsorption Capacity for Regenerated Material (mg/g)</b>	<b>Elemental Hg Oxidation for Regenerated Material, in Simulation Gas (%)</b>	<b>Elemental Hg Oxidation as Recovered from Site 3, in Simulation Gas (%)</b>	<b>Elemental Hg Oxidation for Fresh Material, in Simulation Gas (%)</b>
Fe #1	0	15	18	88
Pd #1	1	89	72	92

## ***Investigation of Catalyst Deactivation Mechanisms***

Two different types of laboratory tests were conducted to investigate potential mechanisms for catalyst loss of activity at Site 3. One series of tests investigated the leaching of acid species from the catalyst surfaces into deionized water. The resulting leachate was analyzed for pH drop, indicative of overall acid species concentrations, and for anions associated with common flue gas acid gas species (sulfate [sulfuric acid] and chloride [hydrochloric acid]).

In the second laboratory investigation, during the catalyst regeneration tests, the effluent gases were sampled and analyzed to determine if selenium or other chemicals were adsorbed on the catalysts prior to regeneration and may have contributed to their deactivation. Note that selenium appeared to have correlated with decreased oxidation activities of catalyst materials at Site 1, and the Site 3 flue gas was measured to have even higher gas-phase selenium concentrations than at Site 1.

To conduct these analyses, the effluents from the catalyst regeneration tests were passed through a solution of nitric acid and peroxide to capture emitted species. These solutions, as well as a portion of the catalyst solids from before and after regeneration, were sent to a third-party laboratory for analyses of trace metals content.

### ***Leaching of Water-soluble Acids from Catalyst Materials***

Catalyst samples recovered from the long-term test at Site 3 were tested for water-soluble acid content according to a leaching procedure used on samples from all three sites. One gram of catalyst/sand mixture (or of the sand bed blank) was stirred in 30 ml of deionized water, and the equilibrium pH was measured. From the pH value, a water-soluble acid content was calculated, and this acid content was expressed as a quantity of adsorbed SO<sub>2</sub> (assuming SO<sub>2</sub> or SO<sub>3</sub> would be the primary adsorbing acid species at these sites). The results of these acid leaching tests are summarized in Table 4-6. Where the same catalyst type had been tested at the other sites and acid leaching tests were conducted, the results from those sites are also summarized in the table. For the Site 3 samples, additional analyses were conducted that had not been conducted for the samples from Sites 1 and 2: the leachate was analyzed by ion chromatography (IC) for sulfate and chloride ion content. These results are also shown in Table 4-6.

**Table 4-6**  
**Acid Leaching from Recovered Catalyst Samples into Deionized Water**

<b>Catalyst Type</b>	<b>Site 1 Data</b>	<b>Site 2 Data</b>	<b>Site 3 Data</b>			
	<b>Adsorbed SO<sub>2</sub> (mg/g) Estimated from pH Drop</b>	<b>Adsorbed SO<sub>2</sub> (mg/g) Estimated from pH Drop</b>	<b>pH</b>	<b>Adsorbed SO<sub>2</sub> (mg/g) Estimated from pH Drop</b>	<b>Adsorbed SO<sub>2</sub> (mg/g) from IC Data</b>	<b>Adsorbed Cl (mg/g) from IC Data</b>
Sand Blank	0.003	0.045	4.38	0.040	2.9	-
Fe #1	-	-	2.68	39.7	368	1.8
Pd #1	0	-	4.00	1.5	407	3.3
Subbituminous Ash #5	25-41	-	2.74	85.3	346	1.6
Carbon #6	0	35-57	3.60	60.7	305	19.1

The results in the table show that for all three sites, the pH drop for the sand blank samples indicate a negligible amount of adsorbed, water-soluble acid on the sand itself. The pH drop data also show very little water-soluble acid on the Pd #1 catalyst, but significant quantities on the Subbituminous Ash #5 samples (Sites 1 and 3 samples). For the latter, the amount of water-soluble acid on the sample from Site 3 is greater than that from Site 1, which was expected based on the higher coal sulfur content at Site 3. These results are consistent with previous URS tests that have shown higher levels of absorbed leachable acidic species in carbon-derived samples as than in samples not containing carbon.

The Carbon #6 catalyst is the only one for which water-soluble acid leaching data are available from all three sites, and these data show inconsistencies. The Site 3 sample showed the highest content of water-soluble acid, as would be expected. The Site 2 sample showed the next highest quantity, ranging from about 60% of the Site 3 value in the upstream bed to over 90% of the Site



3 value in the downstream bed of two in series. The Site 1 sample, which was exposed to flue gas with SO<sub>2</sub>, SO<sub>3</sub> and HCl contents between those of Sites 2 and 3, showed essentially no water-soluble acid. Thus, these data do not follow the expected order based on the sulfur and/or chloride contents of the coals fired at these sites. However, results at Site 1 indicated that high levels of absorbed selenium may have blocked the carbon surface from sulfur absorption, thus explaining these results.

The sulfate and chloride data for the water leachates of the Site 3 samples are quite surprising, in that the amount of water-soluble sulfates leaching from these samples far exceeds the amount of acid leaching based on the observed pH drop data. Thus, most of the sulfates must be present as water-soluble salts rather than as sulfuric (or sulfurous) acid. In the case of the Pd #1 sample, even the chloride content exceeds the amount of acid potentially present as HCl based on the pH drop data (not shown in the table), indicating the chlorides must be present as salts, too.

It is clear from these data that the catalyst materials adsorb water-soluble acids, sulfates and/or chlorides from the flue gas treated in varying amounts. It is less clear, though, whether this adsorption has any relationship with catalyst activity or loss of activity with time. For example, the Fe #1 catalyst, which saw the greatest loss of activity in the long-term test at Site 3, tended to fall in the middle of the range of samples with respect to the amount of adsorbed water-soluble acid species, sulfates, and chlorides. If there were a relationship with loss of activity, we would have expected the Fe #1 results to fall at one extreme (high or low) for one of these parameters.

The same water leaching procedure was conducted on fly ash samples from Site 3, in an effort to confirm CCS results from January 2001 (see Table 3-19). Those results showed about a 60 to 80% drop in the concentration of sulfuric acid in the flue gas when comparing air heater inlet and outlet samples. Fly ash samples collected during Ontario Hydro sampling at these locations were analyzed according to the water leaching, pH drop and anion analysis protocol described above, to determine whether a substantial increase in the sulfate content of the ash was noted across the air heater. ESP hopper fly ash samples were also analyzed. The results are summarized in Table 4-7. The sulfur species concentrations are reported in terms of adsorbed SO<sub>2</sub>, to be consistent with previous reporting of catalyst material concentrations from Sites 1 and 2, although in this case it is expected that the sulfur species are all present as sulfates.

The results in Table 4-7 show very little adsorbed acid. It is expected that adsorbed acid species have reacted with calcium, magnesium, and other metals in the ash to form neutral salts. The results do show that, as expected, the sulfate concentrations in the air heater outlet ash leachates were considerably higher than those in the air heater inlet ash leachates. This appears to confirm the CCS results, which indicated substantial removal of gas-phase sulfuric acid across the air heater. The increase in sulfate content in the air heater outlet samples relative to that in the inlet samples more than accounts for the observed drop in gas-phase sulfuric acid concentration between these two locations.

Ash samples were collected during Ontario Hydro method sampling at these locations, as mentioned above. The Ontario Hydro method samples the flue gas isokinetically, so the ash samples are expected to be representative of the loading and size distribution that was present in the gas sampled, but the fly ash is filtered from the sample gas in a filter holder maintained at approximately 250°F. There was concern that the leachable sulfates measured for these samples

**Table 4-7**  
**Acid Leaching from Site 3 Fly Ash Samples into Deionized Water**

Catalyst Type	pH	Adsorbed SO <sub>2</sub> (mg/g) Estimated from pH Drop	Adsorbed SO <sub>2</sub> (mg/g) from IC Data	Adsorbed SO <sub>2</sub> (ppm in Flue Gas) from IC Data	Adsorbed Cl (mg/g) from IC Data
ESP Hopper Ash, 1/24/01	8.59	0.00	3.5	14	0.06
ESP Hopper Ash, 1/26/01	5.66	0.00	2.3	9	0.19
Air Heater Inlet Ash, 1/26/01 (Run 1)	6.89	0.00	3.0	12	0.14
Air Heater Inlet Ash, 1/26/01 (Run 2)	4.57	0.03	4.6	18	0.06
Air Heater Outlet Ash, 1/26/01 (Run 1)	4.41	0.08	10.6	41	0.13
Air Heater Outlet Ash, 1/26/01 (Run 2)	4.17	0.13	11.1	43	0.05

was biased high by the filter possibly being maintained below the acid dew point, thus resulting in condensed acid mist being collected on the filter.

However, the actual filter hot box temperatures were somewhat higher than 250°F during these measurements, and did not likely impact the leachable sulfate measurements. During the air heater inlet location sampling, the filter hot box temperature averaged about 273 to 274°F, which is slightly below the calculated acid dew point at this location of 277°F based on sulfuric acid concentrations measured the day before (although for a coal with a higher sulfur content). It is possible that a small amount of sulfuric acid condensed and was collected on the filter (2 or 3 ppm at most). For the air heater outlet location, though, the filter hot box temperature averaged 280°F, which is well above the calculated acid dew point at that location.

Although it does not appear that collection of condensed acid mist greatly affected these leachable sulfate results, it remains possible that these samples were biased somewhat by adsorption of gas-phase sulfuric acid from the sample gas as it passed through a fixed bed of fly ash on the filters. This may explain why the air heater outlet samples, which should be equivalent to the material collected in the ESP, show much higher sulfate concentrations than the ESP hopper samples in Table 4-7. It is also possible, though, that the randomly collected ESP hopper samples are not representative.

### **Trace Metals Analyses of Recovered and Regenerated Catalysts**

The catalyst materials recovered from the long-term test at Site 3 were analyzed for trace metal concentrations. These analyses were conducted to determine if relationships could be established between adsorbed trace metal content and deactivation. The results of these analyses are summarized in Table 4-8. The concentrations shown are as measured for the sand bed/catalyst mix. Assuming the metals are actually adsorbed on the catalyst materials and not on the sand, the concentrations in the catalysts themselves would be much higher than the values shown in Table 4-8.

**Table 4-8**  
**Trace Metal Concentrations in Catalyst/Sand Beds Recovered from Site 3 Long-term Test**

Trace Metal	Fe #1, mg/kg of Sand Bed	Pd #1, mg/kg of Sand Bed	Subbituminous Ash #5, mg/kg of Sand Bed	Carbon #6, mg/kg of Sand Bed
Al	131	11,500	389	233
Sb	2.98	<0.272	<0.249	0.125
As	<0.122	0.410	0.240	0.622
Ba	0.559	0.318	19.5	0.593
Be	0.0174	0.00957	0.0195	0.0137
Cd	0.241	<0.019	<0.017	<0.019
Ca	288	31.0	500	39.6
Cr	1790	0.863	0.922	1.62
Co	1.00	0.267	<0.039	1.27
Cu	17.0	2.14	0.850	0.921
Fe	21,200	71.2	174	100
Pb	12.1	0.411	0.643	0.529
Mg	77.2	19.3	106	27
Mn	130	0.240	0.515	0.992
Mo	<0.075	0.627	<0.073	0.119
Ni	16.8	0.632	0.274	1.94
K	9.66	12.0	15.7	20.6
Se	144	59.0	62.9	1.34
Ag	<0.092	<0.099	<0.091	<0.101
Na	177	<42.3	110	181
Sr	2.35	1.44	10.7	1.64
Tl	<0.158	<0.170	<0.155	<0.173
Ti	2.62	17.8	22.0	12.6
V	0.273	0.207	0.632	0.209
Z	384	14.1	0.599	64.9

The metals most prevalent on the recovered catalysts are selenium, and metals commonly associated with fly ash (aluminum, calcium, iron, magnesium, potassium, and sodium). These are also the metals that were most prevalent in the Site 3 flue gas as measured by Method 29 (see Table 3-19), so it might be expected that these metals would be adsorbed on the catalyst materials. Only thallium was found in significant concentrations in the Site 3 flue gas (8 ppb) but not adsorbed on any of the catalysts to a significant concentration. The Fe #1 also had significant concentrations of other metals, which were most likely incorporated into the base catalyst metal. Besides iron and chromium, these included copper, lead, manganese, nickel and zinc.

As mentioned above, regeneration tests were carried out on both the Pd #1 and Fe #1 catalysts. As part of this testing, the regeneration gas exiting the bed was passed through impinger solutions to recover metal species evolving from the catalyst surfaces. Trace metals analyses were conducted on these impinger solutions, as well as on samples of the catalyst solids from after the regeneration process. These analyses were conducted to determine if relationships could be established between desorption of metals and restored activation.

Similar analyses were conducted on the recovered and regenerated catalysts from Site 1. Those analyses indicated that selenium and sulfur were the two main species adsorbed by the catalyst/sand mixtures, and that those species desorbed on regeneration<sup>2</sup>. While it could not be concluded what species most contributed to catalyst deactivation at Site 1, it was speculated to be selenium or sulfur, or both.

For the catalysts from the long-term test at Site 3, the amounts of sulfur adsorbed by the catalysts were quantified by the acid leaching procedure described in the previous subsection. The amounts of selenium and other metals that desorbed on regeneration were quantified by the trace metals analyses described above. The results from those analyses are presented in Table 4-9.

Trace quantities are shown for the original catalyst/sand mixtures recovered from the long-term test at Site 3, for the regenerated material, and for the impinger catches from the regeneration gas. Metals material balance closures are shown in terms of the total amount recovered after regeneration (regenerated solids plus impinger catch) compared to the amount measured in the catalyst prior to being regenerated. The percent closures are within  $\pm 20\%$  for about 2/3 of the metals for which the solid phase analyses were above detection limits, which is relatively good closure for trace metals analyses. The other thing to note in the table is that, like the metals found in the highest concentrations on the recovered catalysts, those found desorbed in the impinger solutions are selenium, alumina, calcium, iron, magnesium, potassium, and sodium.

The previous Site 1 results showed that selenium was the most prevalent adsorbed metal species on deactivated catalysts, and that selenium readily desorbed on regeneration. It was speculated that selenium might play a role in catalyst deactivation mechanisms. However, a comparison of catalyst activity at the end of the long-term tests versus the amount of selenium adsorbed on each catalyst does not readily support this hypothesis. This comparison is made for the long-term test catalysts from Sites 1 and 3 in Table 4-10. The catalyst activity data are somewhat confounded, though, because of measurement issues at the end of the long-term tests at both of these sites that interfered with the ability to accurately measure catalyst activity in the field. The activity measured for the recovered materials in the lab, on simulated flue gas, is also shown in the table. However, since the simulation gas does not contain selenium and selenium may have desorbed from the catalyst during these activity tests, the lab activity results may not be meaningful for this comparison.

Several inconsistencies are noted in the results summarized in Table 4-10. First, the adsorbed selenium concentrations are higher in the catalysts recovered from Site 1, in spite of the fact that Method 29 measurements showed higher selenium concentrations in the flue gas at Site 3. The catalyst concentration data are supported by anecdotal observations that the desorption gas turned downstream tubing and glassware pink during the Site 1 catalyst regeneration tests (an indicator of high selenium concentrations), whereas this phenomenon was not observed for the

**Table 4-9**  
**Trace Metals Analyses of Site 3 Catalysts – Pre and Post Regeneration**

Trace Metal	Fe #1				Pd #1			
	After Long-term, mg/kg	Regenerated, mg/kg	Impinger mg/kg	Mass Balance Closure (regen/prior)	After Long-term, mg/kg	Regenerated, mg/kg	Impinger mg/kg	Mass Balance Closure (regen/prior)
Al	131	205	0.53	157%	11500	8210	1.66	71%
Sb	2.98	2.75	<.01	93%	<0.272	<0.275	<0.011	-
As	<0.122	<0.112	<.01	-	0.410	0.498	<0.007	123%
Ba	0.559	0.74	0.004	133%	0.318	0.264	0.01	88%
Be	0.0174	0.0112	<0.0002	65%	0.00957	<0.004	<0.0002	<48%
Cd	0.241	0.287	0.01	122%	<0.019	<0.019	0.004	-
Ca	288	291	1.76	102%	31.0	18.8	1.92	67%
Cr	1790	1630	0.01	91%	0.863	0.846	0.02	100%
Co	1.00	0.939	<0.002	94%	0.267	0.237	<0.002	90%
Cu	17.0	15.7	<0.001	92%	2.14	1.07	0.01	51%
Fe	21200	19100	0.09	90%	71.2	58.1	0.61	82%
Pb	12.1	10.7	0.04	89%	0.411	0.364	0.01	90%
Mg	77.2	84.5	0.11	110%	19.3	10.8	0.32	58%
Mn	130	117	0.01	90%	0.240	0.265	0.01	115%
Mo	<0.075	<0.068	0.01	-	0.627	0.432	<0.004	69%
Ni	16.8	15.9	0.02	95%	0.632	0.569	0.08	103%
K	9.66	12.5	<.05	130%	12.0	9.4	0.67	84%
Se	144	113	22.9	94%	59.0	40.5	1.41	71%
Ag	<0.092	<0.085	<0.002	-	<0.099	<0.1	0.003	-
Na	177	247	3.16	141%	<42.3	<42.9	6.73	-
Sr	2.35	2.7	0.005	115%	1.44	1.15	0.01	80%
Tl	<0.158	<0.145	<0.011	-	<0.17	0.215	<0.012	>133%
Ti	2.62	3.94	0.01	151%	17.8	14.3	0.07	81%
V	0.273	0.319	<0.002	117%	0.207	0.0868	<0.002	43%
Z	384	362	0.14	94%	14.1	9.79	0.17	71%

**Table 4-10**  
**Comparison of Selenium Concentrations for Catalyst Materials from Long-term Tests at Sites 1 and 3**

Catalyst Type	Long-term Test Site	Selenium in Flue Gas, ppb	Selenium Adsorbed on Catalyst, mg/g catalyst	Catalyst Activity at End of Test, % Oxidation of Elemental Hg	
				Field Result	Lab Result
Pd #1	1	27	8.1	0	80
Subbituminous Ash #5	1	27	4.9	0	24
Carbon #1	1	27	33.8	89*	47
Carbon #2	1	27	36.8	76*	74
Pd #1	3	45	1.5	87**	72
Carbon #6	3	45	0.4	85**	91
Fe #1	3	45	2.9	45**	18
Subbituminous Ash #5	3	45	3.1	-	-

\*Value suspect because of apparent measurement bias.

\*\*November 2000 result; test concluded at the end of January 2001.

Site 3 regenerations. These observations call into question the Method 29 results for gas phase selenium concentration at Site 3 as possibly being biased high. Another possible explanation is that the higher SO<sub>2</sub> levels at Site 3 inhibited the absorption of selenium to the catalyst surface as compared to Site 1.

When the activity data are compared with selenium concentrations, data quality issues make it difficult to determine the impact of adsorbed selenium. For Pd #1, the Site 1 catalyst had over five times the selenium concentration of the Site 3 catalyst. In the field, the Site 1 catalyst had lost all activity (possibly due to a low-temperature excursion), while the Site 3 catalyst remained active (although last measured two months before the catalyst was recovered). To the extent that these are valid comparisons of field performance, the relative activity of these two samples is consistent with adsorbed selenium contributing to loss of activity. In the laboratory results with the recovered field samples, though, the Site 1 catalyst was actually more active than the Site 3 catalyst.

Similarly, the Subbituminous Ash #5 sample from Site 1 had more selenium content than the sample from Site 3. The Site 1 sample showed no activity in the field and low activity in the laboratory at the end of the test. The Site 3 sample could not be measured for activity in the field or in the laboratory, in the field because of high activity by the upstream catalyst bed, and in the laboratory because the sample was adsorbing significant quantities of mercury throughout the activity test. Assuming the Site 3 sample continued to be active, given that it was still adsorbing mercury, the Site 1 versus Site 3 results again support the hypothesis that adsorbed selenium adversely affects activity.

For the other catalyst materials, no two were tested at both sites, so it is not possible to make direct comparisons. It is possible to make some observations from these data. For example, the most active of the Site 3 recovered catalysts, Carbon #6, had the lowest adsorbed selenium content, while the least active, the Fe #1, had almost the highest. In another comparison, the carbons from Site 1 had adsorbed almost two orders of magnitude more adsorbed selenium than Carbon #6 from Site 3, yet they retained some activity towards mercury oxidation. However, since the catalytic oxidation mechanisms may differ among the catalyst types, it may not be meaningful to compare absolute concentrations of adsorbed selenium from one catalyst type to the another.

Table 4-11 compares the selenium desorption results for the two catalysts from Site 3 that were regenerated. Based on the solids analyses from before and after regeneration, the Fe #1 catalyst desorbed about 22% of the adsorbed selenium, while the Pd #1 desorbed approximately 31%. The Pd #1 activity was restored by the regeneration process, while the Fe #1 activity was not, so these data at least directionally support the premise that adsorbed selenium contributes to a loss of activity, while desorbing selenium on regeneration restores activity.

**Table 4-11**  
**Comparison of Selenium Desorption Versus Activity Towards Elemental Mercury Oxidation in Regenerated Site 3 Catalysts**

<b>Catalyst</b>	<b>Selenium in Recovered Catalyst, mg/g catalyst</b>	<b>Selenium in Regenerated Catalyst, mg/g catalyst</b>	<b>Reduction in Selenium Concentration %</b>	<b>Elemental Mercury Oxidation by Recovered Catalyst, % (lab result)</b>	<b>Elemental Mercury Oxidation by Regenerated Catalyst, % (lab result)</b>
Fe #1	2.9	2.3	22	18	15
Pd #1	1.5	1.1	31	72	89

## References

1. Richardson, Dr. Carl F., et al. "Enhanced Control of Mercury by Wet FGD Systems." Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, Atlanta, GA, August 16-20, 1999.
2. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 1 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 1999, TE-113397.
3. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 2 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 2000. 1000558.

# 5

## PRELIMINARY ECONOMICS FOR A CATALYTIC PROCESS

Preliminary cost estimates have been made for the catalytic process under development, for a 400-MW power plant that fires a bituminous coal and has a conventional ESP for particulate control followed by a wet FGD system. The flue gas was assumed to have a total mercury content of  $10 \mu\text{g}/\text{Nm}^3$ , with 75% is oxidized while 25% is in the elemental form (as measured at the ESP outlet). Based on data collected from the EPA mercury ICR, we assumed that upstream of this location approximately 25% of the mercury in the flue gas at this site would be removed with the fly ash across the ESP. We also assumed that a net of 90% of any oxidized mercury in the flue gas would be removed by the wet FGD system.

The catalyst is Pd #1 on a honeycomb support. The catalyst would be installed immediately downstream of the last field of the ESP, where the flue gas velocity would be about 5 ft/sec. The catalyst life was projected to be three years. Pd #1 saw little or no measurable loss of activity in over five months of testing at Site 2 and after three months of testing at Site 3. It remains to be demonstrated what the actual life of this catalyst will be. The catalyst loading on the honeycomb cores was assumed to be the value tested in the honeycomb configuration at Site 3. This value was three times higher in palladium loading than what was tested in a honeycomb configuration at Site 2.

Based on the assumptions listed above, the oxidation catalyst would have to achieve approximately 25 to 30% oxidation of the elemental mercury in the ESP outlet gas for the plant to achieve 80% overall mercury removal, and 85% to 90% oxidation for the plant to achieve 90% overall mercury removal. Although we do not yet have reliable information about the relationship between area velocity and elemental mercury oxidation percentage, for these preliminary estimates we have used a simple mass transfer model to predict catalyst performance. The predicted catalyst performance was based on the model prediction for mass transfer, corrected for the observed relationship between the model prediction and the actual honeycomb catalyst performance at Site 3. It was estimated that a 6-inch catalyst depth would result in 85% to 90% oxidation of the elemental mercury at the ESP outlet and that a 2-inch catalyst depth would result in well over 30% oxidation. However, for the latter case, it was assumed that it would not be feasible or worthwhile to install catalyst at a bed depth of less than 2 inches. These catalyst depths correspond with area velocities of 80 and 240 standard ft/hr, respectively.

The projected costs for this process were compared to cost estimates for activated carbon injection for mercury control, as presented in a previous EPRI-sponsored paper<sup>1</sup>. In that paper, it was determined that it was more cost effective to retrofit a high-ratio fabric filter downstream of the ESP (i.e., the EPRI COHPAC configuration) when injecting activated carbon for mercury control. Their estimates showed that prohibitively large quantities of carbon were required to achieve high mercury removal efficiency with only the ESP as a gas-solid contactor. That paper presented cost estimates for an 80% mercury removal level, but we used data and cost equations



presented in the paper to project costs for the removal levels required to achieve 80 and 90% overall mercury removal with carbon injection.

We assumed the same baseline 25% removal of mercury across the ESP with no carbon injection, and we assumed that downstream of any carbon injection, the ratio of oxidized to elemental mercury would remain 75 to 25%. We also assumed the same 90% removal of oxidized mercury across the FGD system as described above. With these assumptions, about 40% mercury removal upstream of the FGD system would be required for the plant to achieve 80% overall mercury removal, and 70% removal upstream of the FGD for the plant to achieve 90% overall mercury removal.

For our calculations, we first estimated the carbon injection required to achieve these mercury removal levels for injection upstream of the existing ESP, then we estimated the carbon injection required to achieve these removal levels with a COHPAC pulse-jet fabric filter downstream of the ESP. In the latter case, the removal by the fly ash in the ESP and by carbon in the fabric filter were assumed to be additive, such that the required removal levels at the fabric filter were reduced to 20% and 60%, respectively, for the 80 and 90% overall removal cases.

We also used the same economic factors and plant descriptions used in the EPRI paper in developing preliminary estimates for the catalytic process. These estimates for capital, operating and maintenance (O&M) and levelized costs are compared for 80 and 90% overall mercury removal levels in Table 5-1.

As in the EPRI paper mentioned above, in our estimates we found that for carbon injection, it would be more cost effective to retrofit a COHPAC fabric filter as a gas/carbon contactor rather than inject greater quantities of carbon upstream of the ESP. It was somewhat surprising that these preliminary economics showed this to be the case even where the required mercury removal upstream of the FGD system was only 40%. Note that the capital cost estimates for the catalytic process do not include the cost of the initial catalyst charge. The catalyst cost is instead treated as an O&M expense, since it must be replaced every three years.

The preliminary results in Table 5-1 show that the catalytic process holds some promise for lowering future mercury control costs for power plants with existing FGD systems, particularly those that do not have space available to retrofit a COHPAC fabric filter between the existing ESP and the FGD system. The catalytic process particularly looks attractive for the 80% mercury removal case. Future process development work is needed to substantiate and refine the assumptions made to develop these cost estimates. Longer catalyst life will tend to drive the costs down. Also, less expensive catalysts, such as fly-ash-based or carbon-based catalysts, will tend to lower costs.

**Table 5-1****Preliminary Cost Estimates for the Catalytic Process for Enhancing Mercury Removal by a Wet FGD System, Compared to Activated Carbon Injection**

<b>Mercury Removal Process</b>	<b>Catalyst</b>		<b>Carbon Injection/COHPAC</b>	
Overall Hg Removal (%)	80	90	80	90
Required Elemental Mercury Oxidation Across Catalyst (%)	26	87	-	-
Required Mercury Removal Across Fabric Filter (%)	-	-	18	59
Total Capital Requirement (\$1000; excludes catalyst costs)	\$1,949	\$1,949	\$15,820	\$15,837
Levelized Capital Requirement (\$1000/yr)	\$199	\$199	\$1,614	\$1,615
Total O&M Cost (\$1000/yr)	\$710	\$2,125	\$1,154	\$1,406
Levelized O&M Cost (\$1000/yr)	\$1,064	\$3,188	\$1,731	\$2,109
Total Levelized Cost (\$1000/yr)	\$1,263	\$3,387	\$3,345	\$3,725
Percent reduction (relative to carbon injection/COHPAC)	62%	9%	-	-

**References**

1. Meserole, F.B., et al. "Estimating Electric Utility Mercury Control Costs Using Sorbent Injection." Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, Atlanta, GA, August 16-20, 1999.

# 6

## SUMMARY

Field testing at Site 3, fired with a blend of Pennsylvania and West Virginia bituminous coal, found relatively low concentrations of elemental mercury in the flue gas ( $\sim 1$  to  $7 \mu\text{g}/\text{Nm}^3$ ) at the FGD inlet test location. Moderate concentrations of  $\text{SO}_2$  (1600 to 1700 ppm),  $\text{SO}_3$  (3 to 6 ppm), and HCl ( $\sim 70$  ppm) were measured there;  $\text{NO}_x$  concentrations were not measured.

Total mercury concentrations in the FGD inlet flue gas were measured to be quite variable, ranging from less than  $10 \mu\text{g}/\text{Nm}^3$  to greater than  $20 \mu\text{g}/\text{Nm}^3$ . The variability appears to be due to variation in coal mercury content and other coal quality parameters. The coal fired at Site 3 comes from a variety of sources. The fly ash produced in the Site 3 boiler typically has a high LOI (uncombusted carbon) content, and appears to result in significant mercury capture across the air heater and ESP. Much of the variation in FGD inlet total mercury concentrations may be due to coal or boiler operation impacts on fly ash LOI and mercury removal across the air heater and ESP.

Long-term (six-month) sand bed reactor tests were conducted, but due to a host site boiler outage and an apparent problem measuring elemental mercury concentrations in the flue gas, catalyst performance data are only available for three months of continuous flue gas exposure. These results showed that at these bituminous coal flue gas conditions, two catalysts, Pd #1 and Carbon #6, continued to oxidize at least 85% of the inlet elemental mercury. The performance of a fly-ash-based catalyst could not be measured because of continued high activity in the catalyst bed upstream in the test apparatus. The fourth catalyst, Fe #1, had lost about half of its initial activity towards the oxidation of elemental mercury over this period.

It remains unclear what caused the apparent bias for measuring low elemental mercury concentrations in the flue gas flowing through the long-term test apparatus. Ontario Hydro method sampling of the Site 3 flue gas in January 2001 showed that the flue gas elemental mercury concentrations were in the range of  $3$  to  $4 \mu\text{g}/\text{Nm}^3$ , while the gas flowing through the long-term test apparatus showed less than  $1 \mu\text{g}/\text{Nm}^3$ . The latter was measured with the EPRI semi-continuous mercury analyzer rather than by the Ontario Hydro method. However, it was not determined whether the discrepancy was due to analytical bias or actually represented a bias in the oxidation fraction of the gas flowing through the test apparatus compared to that of the bulk flue gas at this location.

Because of the apparent measurement bias, the only data for performance of the catalyst materials at the end of the six-month period are from the laboratory testing of recovered materials in a simulated flue gas environment. The laboratory results showed continuing high activity for Carbon #6, but suggest that the Pd #1 material had begun to lose activity by the end of the test. The measured oxidation percentage of elemental mercury across the recovered Pd #1 bed was 72% compared to 87% in the field two months earlier. However, the lab measurement is confounded by the fact that the simulation gas does not contain all of the trace metals present in the actual flue gas. Also, the activity of the Pd #1 bed may have been adversely affected by a

flow blockage in the long-term test apparatus that resulted in this bed being exposed to a stagnant flue gas atmosphere for over a month.

The three-month data mentioned above remain the most reliable information about the long-term test activity of the Pd #1 catalyst. These results indicate that Pd #1 and Carbon #6 would be the most attractive oxidation catalysts for this bituminous coal flue gas, considering activity and catalyst life. The Pd #1 catalyst was also the most attractive catalyst material for Site 2, and it has the advantage of being commercially available in honeycomb forms that are commonly used in flue gas service. Carbon #6 could offer a lower-cost alternative to the palladium catalyst for this flue gas environment, but some development work is required to prepare this material in a commercial catalyst form.

Subbituminous Ash #5 might also be an effective catalyst material in this flue gas. However, since the upstream bed of Carbon #6 remained active throughout the test period, it was not possible to evaluate the performance of this material during the long-term test.

Since Pd #1 is conventional, metal-based catalyst that is readily available from catalyst vendors, samples prepared in a commercially available honeycomb form were tested at Site 3 in parallel with the long-term sand bed reactor tests. In relatively short-term (e.g., two-day) tests, mercury oxidation percentages of 70% or greater was measured at area velocities 3 to 11 times that of commercial SCR catalysts, which suggests that relatively small reactors could be employed for a catalytic mercury oxidation process. The Site 3 results with the honeycomb catalyst form confirmed previous laboratory results that a three-times higher palladium loading on the substrate would improve honeycomb oxidation activity over what was measured at Site 2. These results also provided further indication that a simple model for calculating mercury mass transfer rates from the flue gas to the honeycomb surface can be used as a tool for predicting honeycomb catalyst performance.

Laboratory tests to regenerate activity in catalyst materials recovered from the long-term test at Site 3 showed that the Pd #1 activity could be readily restored by purging the catalyst with nitrogen at 700°F. This procedure was not effective at restoring the activity of the Fe #1 catalyst.

A related laboratory effort attempted to determine catalyst deactivation mechanisms by measuring what acid gas species could be leached from the recovered catalyst materials into deionized water, and by measuring what metals desorb from the recovered catalysts on regeneration. These results indicated that sulfates and chlorides could be leached from the catalyst materials, indicating the adsorption of SO<sub>2</sub>, SO<sub>3</sub> and/or HCl by the catalysts during the long-term test. They also determined that appreciable quantities of selenium desorb from the catalyst materials on regeneration in nitrogen at 700°F. However, no clear link could be established between the presence of these species adsorbed onto the catalyst materials and their impact on catalyst activity for elemental mercury oxidation.

Preliminary economics were calculated for the catalytic process applied to a power plant with an existing ESP particulate collector and an FGD system, based on Site 3 results for the Pd #1 catalyst. Those preliminary economics show that using a honeycomb catalyst configuration, the catalytic process could be less costly than carbon injection for achieving 80 to 90% overall mercury control, particularly for plants that lack the space to retrofit a COHPAC fabric filter. The economics for the catalytic process using Pd #1 as the catalyst are very sensitive to catalyst life and to the cost of the precious metal used to prepare the catalyst. Future testing should

attempt to determine the activity of Pd #1 over periods of one year or greater, and should evaluate lower-cost materials such as Carbon #6 in commercial catalyst configurations.

# 7

## ACKNOWLEDGEMENTS

We would like to thank the Site 3 utility for allowing us to test at their power plant and their staff for the support they have provided. We would also like to thank the U.S. Department of Energy National Energy Technology Laboratory and EPRI for their co-funding of this project and for their technical input and guidance.